Department of Geosience; Meteorology and Oceanografi section

Impacts of emissions in India, on climate and air quality

Masterthesis

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ABSTRACT

The emission of ozone precursors as CO, and NO_x has increased over the last decades, this report looks at how this increase potentially could affect the concentration of tropospheric ozone over India. It gives a short introduction in the different sources and sinks of ozone in the troposphere, and how an increase in ozone can affect the radiative forcing. I have perturbed the anthropogenic emissions to a worst case scenario for 2050 to look at how the surface air quality will be affected, and how this increase will affect the radiative forcing, and the surface temperature.

All simulations has been done by Oslo CTM3. This is a three dimensional global chemical transport model (CTM). When calculating the change in radiative forcing and surface temperature I have used equations from the IPCC fourth assessment report, together with the change in ozone concentration, and methane lifetime from the model.

What we see is that the ozone production is highly sensitive to both meteorology, and emission of ozone precursors. Increasing the emission of CO, NO_x and VOC gasses will lead to increased ozone production, high solar radiation increases the chemical production, and also reduces the deposition to the ground.

Increasing the emissions to simulate a worst case scenario for 2050 gives an increase in surface ozone up to 50%, resulting in concentrations as high as 50-70 ppbv over the continents. These concentrations exceeds the World Health Organization (WHO) recommendations for air quality and can damage the vegetation and be dangerous for human health. The large increase in NO_x is also so high that it will exceed the level recommended by WHO in the larger cities.

We also see a increase in the surface temperature as a result of increased concentrations of both ozone and methane in the troposphere. My calculations show that as a result of increased tropospheric ozone there will be a global increase in surface temperature of 0.003 K. And the increase in methane as a result of a decrease in OH concentration will according to my calculations lead to a increase in global surface temperature of 0.0019 K.

This means that if no precautions is taken, and the increase in anthropogenic emissions keeps on increasing the surface pollution will be dangerous for both human and vegetation, and the radiative forcing will be affected.

Acknowledgment

First of all I want to thank my supervisors Terje Berntsen and Frode Stordal for making atmospheric chemistry so much fun, and for making me see that this is what I wanted to continue with when I took Introduction to Atmospheric Chemistry on bachelor level. Thanks for guiding me through this past year, answering all my questions and overlooking all of my spelling errors when handing in texts to you.

Thanks to thank Anne for help with matlab, and all the plotting, my plots would never have looked so good without you. Great thanks to Ole Amund Sovde for helping me understand Oslo CTM3, and for always answering all my stupid questions in ways I understood.

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Chapter 1

Introduction

Human emissions effect on air quality and climate is a well debated subject, and has been exposed to a lot of research over the last decade or two. How and how much human emissions affects the earth is yet to be decided, but one thing do the majority of the researchers agree on, and that is that there is an effect. What the effects are, and how big they are, might not just have one answer, and maybe we never will find out just how much our way of living have affected the climate and air quality we will see in the future. Still there is a lot we do know, and can say something about based on theory, model calculation and observations. South Asia is least study within the different Asian regions, and as it is one of the most highly populated regions in the world the pollution is high. Figure 1.1 shows a map of South Asia, illustrating the high population density over India, and especially further north where there is a belt stretching over from west to east with more than 450 persons pr. square meter. This is not an exact estimate, but it gives a good picture on how many people living there.

Over the last years India has become more urbanized, with a large increase in transportation and industry, which has led to increased emission of several ozone precursors and other pollutants (*Ohara et al.* (2007)). India lies near the equator and the combination of strong solar radiation, and high amount of water vapor, results in large photo-chemical activity, this in combination with the large pollution leads to high ozone concentrations. Ozone is an excellent greenhouse gas (*Brasseur et al.* (1999)), and can in large ground-concentration be very toxic to both humans and agriculture (*Ashmore* (2005)). Studies have shown that at a large number of days the surface ozone concentration in the large city New Delhi has already passed the air quality standard recommended by the World Health Organization (WHO) (*Jain et al.* (2005)). So with a further increase in the industry and transportation emissions, the future ground concentrations of ozone may exceed the WHO air quality standard several places, and also harm the agriculture and food production. If no restriction is introduced, how will this develop into the future? Looking into this might be important to help understanding the consequences of human activity on human health and vegetation.

Increasing the anthropogenic emissions can also effect the surface temperature by changing the radiative forcing. If the emissions of for example methane is increased and got transported up into the free troposphere you could expect a increase in the surface temperature, as methane is a greenhouse gas and traps the terrestrial radiation (*Jacob* (1999)). Ozone is another greenhouse

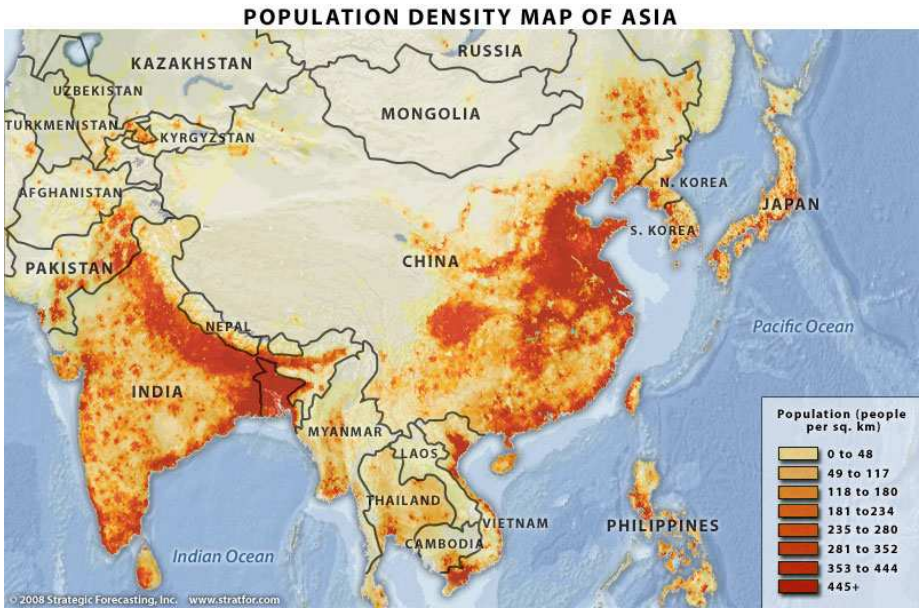

Figure 1.1: Population density map over South Asia. The map is taken from http://www.china-mike.com/wp-content/uploads/2011/01/map-population-asia-china-india.jpg

gas, so when increasing the emissions of ozone precursors, and by that increasing the ozone concentration, this could lead to an increase in the radiative forcing and the surface temperature. But increasing the amount of ozone in the troposphere, will also increase the amount of OH, and as OH is the main sink for methane this could reduce the methane lifetime and concentration (*Logan et al.* (1981)). OH is also the primary removal mechanism for CO (*Logan et al.* (1981)), and reaction with CO can be a sink for OH, canceling out the potential negative effect a decrease in methane concentration could have on the surface temperature.

The chemistry in the troposphere is extremely complex, so how an increase in emissions will affect the composition of the atmosphere is not easy to say. This is one of the many challenges in predicting the future climate and air quality, and the best way to find an answer is by using models. Looking at detailed information over a limited domain a regional climate model is the best choice, these can run with higher resolution, and can by that better catch local effects over for example larger cities (*Brasseur et al.* (1999)). However, these models are not ideal when evaluation the radiative transfer, and potential changes in surface temperature. When doing that, a global model is better, here you don't need to worry about the boundary conditions which can wrongly influence the result, especially with respect to the height profiles. Global models can also be used for looking at surface concentrations, but because of computational limitations these models often uses a much coarser grid, and local effects often drowns in the low resolution.

The purpose of this assignment is to understand the processes behind ozone in the troposphere, both production and destruction, and how an increase in anthropogenic emission potentially will effect the air quality at the surface, and if there will be any change in radiative forcing. Throughout this master theses I will focus on these three main points.

- Understanding the chemical processes related to ozone in the troposphere
- How will an increase in emissions affect the air quality over India
- How will an increase in emissions affect the radiative forcing

To be able to answer these questions I have chosen to run a global chemical transport model (CTM) - Oslo CTM3, using this I can both look at surface concentrations when evaluating the air quality, and the height profiles when discussing the radiative forcing. First I will validate the model, by comparing it to some observations. Then I will perturb the emissions simulating a worst case scenario for the year 2050, and compare this to the original run looking at the change in surface concentrations, and the change of methane and ozone throughout the troposphere evaluating if this might have an effect on the global change in radiative forcing.

Chapter 2

Background Theory

Ozone is a secondary pollutant in the troposphere, meaning it is not emitted directly in to the troposphere, it's either chemically produced, or transported through the tropopause from the stratosphere. In the stratosphere ozone works as a protective layer, protecting the Earth from dangerous UV radiation, while in the troposphere high concentration of ozone may be dangerous for both humans and vegetation. Ozone is also an important greenhouse gas, and is important for the oxidizing capacity of the troposphere. In this chapter I will give a short explanation on how ozone is produced in the troposphere, how local meteorology over India affects the concentration and distribution, and also a little on ozone as a greenhouse gas and the consequences of high ozone concentrations in the troposphere. Note that the chemistry described here is only to give a short introduction in the processes leading to ozone production in the troposphere and it is based on *Jacob* (1999), *Brasseur et al.* (1999) and *Fowler et al.* (2005).

2.1 Ozone production and Destruction in The Troposphere

In this section I will give a short introduction to general ozone production and destruction in the troposphere. Figure 2.1 gives a schematic view of the main sources and sinks of ozone, and annual global fluxes to put it all in perspective. As the figure show, the main source and sink is chemical production and loss, but there is also some transport from the stratosphere and dry deposition.

2.1.1 Chemical Production and Destruction

The two main sources of ozone in the troposphere is transport from the stratosphere, and chemical production. Chemical production is the largest of the two (ca 4500 Tg/y), while transport plays a smaller part (ca 540 Tg/y). The most important chemical species involved in the production of ozone is CO, CH_4, OH, H_2O, $nmVOC$ and NO_x (defined as NO + NO_2), where the concentration of NO_x plays an important role to whether we have a loss or production of ozone. NO_x works as a catalyzer, but in large concentrations it can terminate free radicals and lead to a decrease in the ozone concentration. Over for example oceans the concentration of ozone

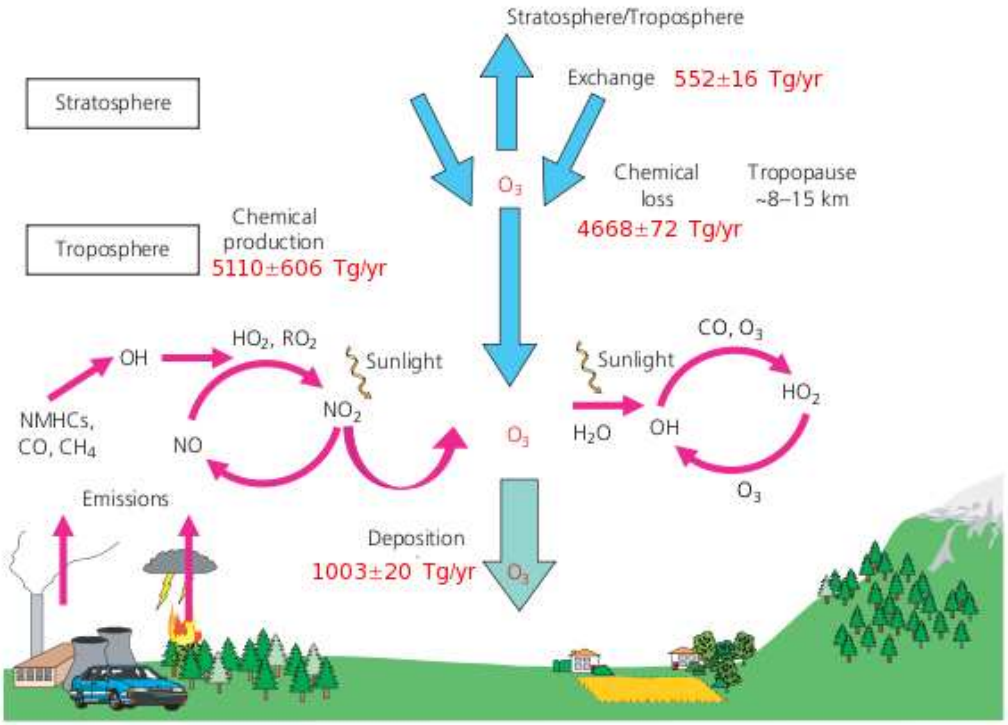

Figure 2.1: A schematic view of the main sources and sinks of O3 in the troposphere. The figure is modified from *Fowler et al.* (2005), annual global fluxes and uncertenties is estimated using 25 models, and taken from *Stevenson et al.* (2006).

precursors is low, and there is a net loss of ozone. In more polluted areas where NO_x and VOC are found in large concentrations, production of ozone is dominant. There are some exceptions, but these will be mentioned later.

In both a low or high NO_x-regime, the production or loss starts with the production of OH:

$$O_3 + hv \rightarrow O_2 + O('D) \tag{2.1}$$

$$O('D) + H_2O \rightarrow OH + OH \tag{2.2}$$

Further we get a reaction between OH and methane, CO or nmVOC, but as this reaction mainly happens with methane rather than a nmVOC this is the compound I will use to illustrate the chemistry. OH is then removed by producing either HO_2 or a proxy radical CH_3O_2, this is what we refer to as regime 1, or a low NO_x-regime:

$$OH + CO \xrightarrow{O_2} CO_2 + HO_2 \tag{2.3}$$

$$OH + CH_4 \rightarrow CH_3 + H_2O \tag{2.4}$$

$$CH_3 + O_2 + M \rightarrow CH_3O_2 + M \tag{2.5}$$

$$CH_3O_2 + HO_2 \rightarrow CH_3OOH + O_2 \tag{2.6}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{2.7}$$

This results in a small loss rate of ozone since the reaction sequence always starts with photolysis of O_3 as seen in eq. 2.1. In addition some of the HO_2 molecules may react further with O_3, and reaction 2.3 and the following creates a catalytic loss of O_3, increasing the loss rate:

$$HO_2 + O3 \rightarrow OH + 2O2 \tag{2.8}$$

When there is NO_x present reaction 2.6 and 2.7 will have some competition, and CH_3O_2 and HO_2 will also react with NO:

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{2.9}$$

$$HO_2 + NO \rightarrow NO_2 + OH \tag{2.10}$$

We refer to this as regime 2, intermediate NO_x-regime, or NO_x limited regime and is the regime we usually find over rural areas of most industrialized countries (*Fowler et al.* (2005)). These reactions produces NO_2, which act as a strong catalyzer producing ozone through the following reactions:

$$NO_2 + hv \rightarrow NO + O \tag{2.11}$$

$$O + O_2 + M \rightarrow O_3 + M \tag{2.12}$$

When we find our self in this regime the ozone production will increase almost linearly with increasing NO_x values until the concentrations of NO_x is high enough to bring us into the third regime called high NO_x-regime, or VOC limited regime. In this regime the NO_x concentration is so high that it's reaction 2.9 and 2.10 that dominate, until the NO_x concentration is so high that it leads to a termination of free radicals:

$$OH + NO_2 + M \rightarrow HNO_3 + M \tag{2.13}$$

The decrease in free radicals leads to less OH available to use in ozone forming cycles, reducing the production rate of ozone. If the emissions of CO and VOC's is high enough, they will compete for OH and the ozone production will continue through reaction 2.3 and 2.4, or a similar reaction cycle for another VOC's. This means that the ozone production now is dependent on the concentration of VOC, as it is the presence of VOC that determine if the production of ozone continues, or the loss of free radicals stops this production, hence the name VOC-limited.

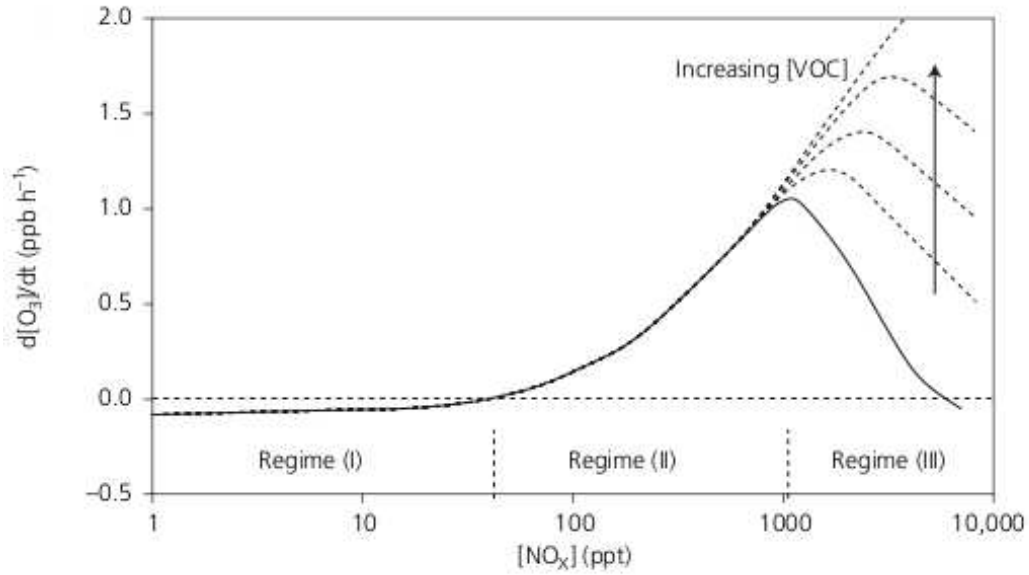

Figure 2.2: Illustration of the NO_x dependence of O_3 production, showing the three different regimes. The figure is taken from chapther 3 in *Fowler et al.* (2005).

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Figure 2.2 illustrate the different regimes and their dependence on the concentration of NO_x and VOC gases.

From this figure it is clear how in regime two the production of ozone increases with increasing NO_x concentration, while in regime three you could get a negative ozone production if the emissions of VOC gasses isn't high enough. This applies to highly polluted areas with large emissions of ozone precursors. On the far right in regime three we see that for low VOC concentration you could actually get a destruction of ozone, this is a local effect typical for polluted urban environments called the NO_x titration effect where you get a reaction between ozone and NO creating NO_2:

$$NO + O_3 \rightarrow NO_2 + O_2 \tag{2.14}$$

But since ozone is produced through photolysis of NO_2 as seen in reaction 2.11 and 2.12, this forms a null-cycle during the day. Because of the strong chemical coupling the term "oxidant" can be used a a collective term for NO_2 and O_3, and both NO_x and oxidant is conserved. As NO_x increases because of emissions it will be partitioned between NO_2 and O_3, with a progressively greater proportion in the form NO_2, and ozone is being titrated out. This complicate control strategies in the areas where this is happening, as the answer isn't just to reduce the emissions of NO_x if not the emissions of VOC's is reduces simultaneously without risking an increase in ozone.

This effect is illustrated well in figure 2.3, where you see the result of a chemical model calculating ozone concentrations over the eastern Unites States plotted as a function of NO_x

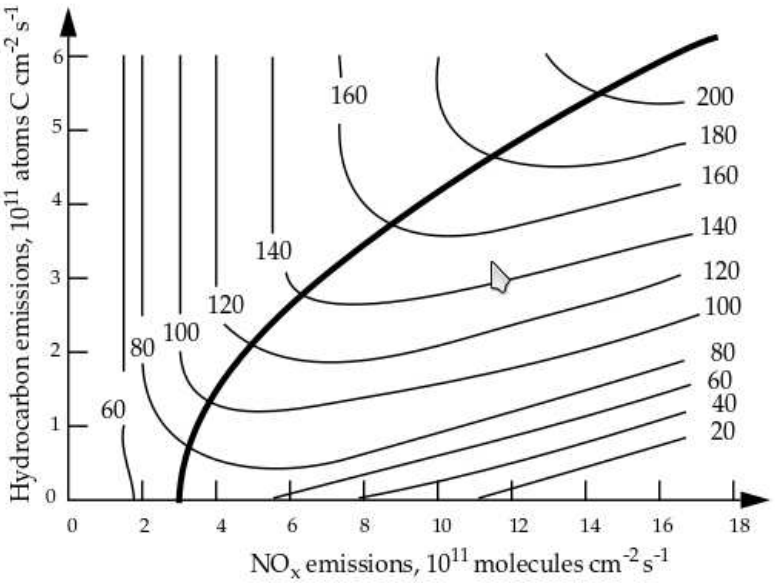

Figure 2.3: Ozone concentrations (ppbv) simulated by a regional photochemical model as a function of NO_x and hydrocarbon emissions. The thick line separates the NO_x-limited (top left) and hydrocarbon-limited (bottom right) regimes. The figure is adapted from *Sillman et al.* (1990).

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and hydrocarbon emissions. Here you clearly see the separation between the two regimes NO_x-limited to the left of the thick line, and VOC-limited to the right. In the VOC-limited regime you can see how the concentration of ozone gets reduced if you only increase the concentration of NO_x, and not VOC's, while in the NO_x-limited regime the ozone concentration increases nearly linearly with increasing NO_x concentrations. This illustrates the challenges with control strategies, as a decrease in NO_x emissions won't decrease the ozone concentration in a VOC-limited regime, this could in fact increase the ozone concentration. Another thing to notice in this figure is in the upper right corner, where the concentration of both NO_x and VOC is very high. Here the increase in ozone is flattening out, and the connection between increase in NO_x or VOC concentration is weaker, meaning that additional increase in NO_x or VOC don't lead to as high increase in ozone as it did when the concentrations where lower. In practice this means that when the emission gets high enough, it reaches a point where the ozone production is flattening out, and smaller perturbations to the emission of ozone precursors won't lead to additional ozone production.

Another important local chemical sink for ozone is Halogen-catalyzed chemistry occurs over oceans and can lead to a rapid decrease in the ozone concentration, this is chemistry we see more of in the stratosphere. The reaction cycle includes halogen atoms and a radical, specifically Bromine (Br) or iodine (I) species, reacting with ozone and resulting in a net loss of ozone. This happens mainly at higher latitudes, and is therefor not that that important over India.

2.1.2 Destruction - Dry Deposition

The main sink of ozone in the boundary layer is dry deposition on to land and ocean. Ozone is not very soluble in water, so the deposition rates are larger on terrestrial surfaces, but as ocean covers approximately 70% of the earth, deposition on to ocean is important in the global budget.

Dry deposition on to land mainly refers to deposition on to vegetation and soil. The dry deposition rates varies with the amount of surface water on the vegetation, wind speed and turbulence. The uptake by plant stomata, also depend on sunlight, temperature, humidity, soil moisture and CO_2 concentration. To protect the plants from desiccation, there is a closure of the plants stomata in dry conditions, and the dry deposition of ozone is then reduced. This means that under high pressure and drought conditions, when we get a stable boundary layer, the ozone production increases as a result of higher incoming solar radiation, and the uptake of ozone on vegetation is reduced we will expect an increase in ozone.

Dry deposition on to ocean is very hard to parameterize as the understanding of the interactions between weakly soluble gases and the ocean is weak, especially under high wind speeds. It's normally parameterized with a fixed deposition rate, but this may lead to large errors as the physical factors may play an important role.

2.2 The Effect of Weather and Climate on The Ozone Concentration in India

As mentioned earlier the weather and climate also have an effect on both ozone production and destruction. India has a rather distinct climate with monsoonal season, creating cloudy and rainy conditions in summer, and dry hot weather in spring and autumn. Hot and dry weather means high incoming solar radiation, and will as mentioned in the previous section increase the ozone concentration as this increases the photo chemical production, it will also reduce the dry deposition if the soil is dry. The highest ozone concentrations will therefore be expected at the time of day and year when the incoming solar radiation reaching the ground is at it highest. Wind will also be able to affect the ozone concentration locally, this is especially true for the coastal regions, where wind can blow fresh ozone-poor marine air in over land, or more polluted air can blow out on to the oceans. Even topography may have a say in the ozone concentration, hill tops, coastal areas and closed valleys have all different characteristic that could affect the ozone concentration with respect to for example airflow and other dynamical features, the meteorology is also largely affected by topography.

To illustrate the connection between meteorology and ozone concentration I found a figure (2.4) that shows 10 m wind vectors plotted together with WRF-chem simulated ozone concentrations for the four seasons in 2008 (*Kumar et al.* (2012)). The ozone concentrations is only simulated values, and not observations but during validation of the model it has shown to estimate pollution and ozone over India fairly good, meaning that these values probably gives a good picture of the actual concentrations (*Kumar et al.* (2012)). This figure gives a good picture on how much the weather and climate affect the ozone concentration.

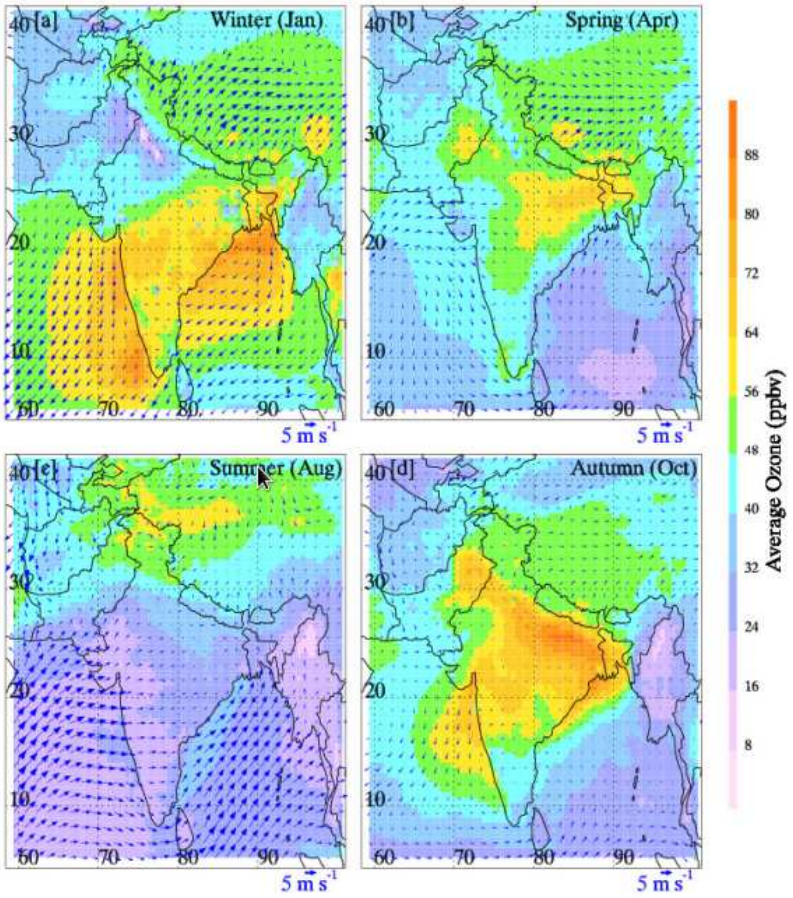

Figure 2.4: Spatial distribution of WRF-Chem simulated surface ozone during January, April, August and October of the year 2008. Monthly mean 10 m wind vectors are also shown. Figure is taken from *Kumar et al.* (2012).

During winter you get low ozone concentration in the north due to low incoming solar radiation, and titration of ozone due to high NO_x concentrations and less solar radiation. Increased concentrations over the ocean is due to the winds blowing offshore, transporting more pollution produced over land out over the oceans. The concentration offshore is higher than those over land, this is partly because of the shallow marine boundary layer which is less turbulent, and therefore suppresses the ventilation and reduces the dry deposition which is already weaker compared to over land, further (*Kumar et al.* (2012)). Another explanation for these high values over the ocean is the absence of NO_x sources, which lead to a lower chemical destruction compared to the coastal cities (*Ojha et al.* (2012)).

In spring the wind patterns changes to onshore, and the high ozone concentrations over the coast and sea is strongly reduced due to the now clean marine air masses that blows in. The values stay high in the east, and increases in the north due to stronger solar radiation, and therefor higher ozone production. These values may be underestimated due to an underestimation of NO_x and

CO values (*Kumar et al.* (2012)).

The summer monsoon with cloudy and rainy weather reduces the incoming solar radiation, and therefore also reduces the ozone production, in addition the dry deposition will increase as described above. This, in combination with the clean marine air masses that blows in from the ocean results in the low ground concentrations of ozone. Another result of the monsoonal circulation and the increased solar radiation during summer is increased convective mixing, which means that we will get more vertical mixing and the emission and pollution at the surface will mix higher up in the troposphere.

Autumn values are the highest during the entire year, the reason for this is the wind patterns is again changing from onshore to offshore, and the high incoming solar radiation. The Indo-Gangetic Plain (IGP) is the 7 most polluted area, and have therefore also the highest ozone concentrations.

These simulations, and this figure only represent one year (2008), this was a year with a relatively powerful monsoonal season, meaning it rained more than average (*IMD* (2009)). If the situation will be very much different for a year with less rain, and more so called monsoonal breaks, where it stops raining for a period is yet to be researched, and could be interesting for future research.

2.3 Greenhouse Gasses

The concentration of greenhouse gases in the atmosphere has increased since preindustrial time, this has several consequences for the environment, and it is large uncertainties in how much this already have and will affect the climate in the future. The reason for this is the complexity of the impact these greenhouse gasses have on for example the surface temperatures and is dependent on complex feedback processes which is not yet fully understood, or fully represented in any climate model.

How well a gas serves as a greenhouse gas dependence on the concentration of each gas, how much of the gas that is already present in the atmosphere, and also for which wavelength the gas absorbs. If the concentration already is large in the center of the absorption band, or the gas absorbs a wavelength that is already absorbed by for example clouds or other gases, an increase will not affect the greenhouse effect that much. At which height in the troposphere the gas is present plays also an important role.

As shown in section 2.1, if you increase the amount of NO_x and VOC's in the troposphere, the concentration of ozone will in general increase. Ozone is a very efficient greenhouse gas as its main absorption line lies in the middle of the atmospheric window at 9,6 micrometers. This means that an increase in the ozone concentration may lead to increased greenhouse effect, and higher surface temperatures. How well ozone works as a greenhouse gas, and how much it effects the surface temperature depends on where in the troposphere the potential increase or decrease in ozone is located *Lacis et al.* (1990). Ozone close to the ground is dangerous to humans and vegetation (*Ashmore and Bell* (1991), *Ashmore* (2005)), but has a small effect on the radiative forcing, and therefor a minimal effect on the surface temperature. A study from 1997 concluded that with a 10% increase in ozone in each layer in the troposphere, it's the change between 7-20

km height that has the largest effect on the surface temperature (*de F. Forster and Shine* (1997)). Meaning that a increase in ozone in middle or upper troposphere, will have a positive effect on the surface temperature, and a increase further down has a smaller effect.

Another important consequences from an increase in ozone is as section 2.1 also shows, that photolysis of ozone, produces O('D) atoms which reacts further with water vapor and produces OH. This means that an increase in ozone concentration will lead to an increase in OH as there will be more ozone available to produce O('D). For methane, another important greenhouse gas, reacting with OH works as an important sink, meaning that increased concentrations of ozone can lead to decreased concentrations for another important greenhouse gas. Methane can react in several ways in the troposphere, but one of the possibilities is the a reaction sequence leading to the following net reaction (*Jacob* (1999)):

$$net : CH_4 + 10O_2 \rightarrow CO_2 + H_2O + 5O_3 + 2OH \tag{2.15}$$

This is the net reactions in a high-NO_x regime, starting off with oxidation of CH_4. We get a net production of ozone where NO_x and OH act as catalysts, and we looses methane.

Increasing the concentration of OH could then increase the number of methane molecules being consumed, and also increase the ozone production. Other larger hydrocarbons may follow this same type of chain mechanism , but these other compounds have smaller global sources and are therefor less important than CH_4 for global troposphere chemistry (*Jacob* (1999)). But as the emissions of other anthropogenic sources increases this can also lead to a loss of OH, as reactions with both CO other hydrocarbons can act as a sink for OH.

Methane has long lifetime, and when running short CTM calculations any potential change in methane concentration won't get taken into account, and a change in methane concentration affects the ozone production. This change in ozone concentration which won't get included in my model calculation is called "primary-mode ozone". There is a lot of direct and indirect effects that needs to be taken into account, and there are also several feedback processes that could play an important role in evaluating the role of the net effect of the different greenhouse gasses and other pollutant in the troposphere. Many of these don't get picked up on by models, so it is important to be aware of their existence when looking at the results.

2.4 Pollution Over India

Over the last years the anthropocentric emissions over Asia has increased substantially as a result of rapid industrialization, population growth, urbanization and increased agricultural activities and transportation. This has led to increased emissions of several pollutants, including all the ozone precursors, which again affects the amount of ozone in the troposphere. One study indicate a growth of 176% in NO_x emissions, 64% for CO and 108% for VOC over Asia between 1980 and 2003 (*Ohara et al.* (2007)), and as India has kept on developing, these values has probably just kept on increasing. When the concentration of ozone precursors is more than doubled the last 30 years, there is no doubt that this also will affect the ozone concentrations, and also the air quality over India. But some measures have been implemented by for example vehicle emission control, trying to reduce emissions through better motors and fuel efficiency standards (*Bansal*

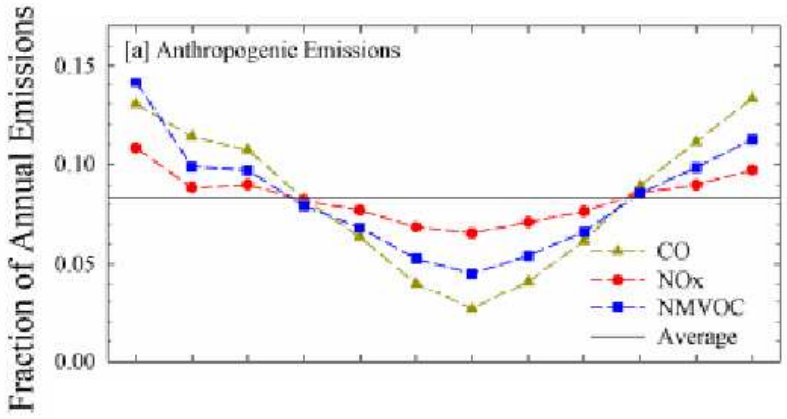

Figure 2.5: Sesonal variation in anthropogenic emissions. The figure is taken from *Kumar et al.* (2012)

and Bandivadekar (2013)). The spatial distribution of the pollution is also important, both with respect to the production of ozone, and also with respect to the consequences ozone has on both human health and radiative forcing.

To give picture of how the emissions variate with season I have included a figure from *Kumar et al.* (2012) (2.5), which shows the seasonal variation in emissions. These emissions is based another emission scenario than used in this assignment, but it gives a general picture on how the anthropogenic emissions variate with season. And as the figure shows, the highest emissions is seen during winter.

Chapter 3

Method

For this study I have used a Chemical Transport Model (CTM), for simulating tropospheric chemistry. It exist a great many of these kinds of models, all with different advantages and disadvantages, strengths and weaknesses. Some may be able to run with very high resolution, but runs very slow an can only be used to look at short timescales or limited geographical area, while other might be faster but uses a coarser grid. Some calculates the meteorology simultaneously and take for example into account changes in radiative forcing when calculating the chemistry, while other runs off-line and uses "old" meteorological data. The "online" WRF-Chem is one example of a regional model (*Grell et al.* (2005)), or MOZART 4 (Model for Ozone and Related chemical Tracers version 4), a offline global CTM (*Emmons et al.* (2010)).

I have used the Oslo CTM3 model, a three dimensional global chemical transport model developed at the Department of Geoscience at the University of Oslo (UiO), and later at the Center for International Climate and Environmental Research - Oslo (CICERO) (*Berntsen and Isaksen* (1997) and *Sovde et al.* (2012)). In this chapter I will give a short introduction to the model, and the set ups I have used when running it. For more information about the model, and the theory behind it I refer to the models unofficial homepage: http://folk.uio.no/asovde/osloctm3/index.html.

3.1 Model Description

The Oslo CTM3 is an off-line chemical transport model, and is driven by 3-hourly meteorological forecast data from the European Center for Medium-range Weather Forecasting (ECMWF) Integrated forecast system (IFS). It has comprehensive chemistry schemes for both the troposphere and stratosphere, but it is possible to run without the stratosphere scheme. The standard resolution for the model is L60T42, which means it uses 60 vertical levels, and 128 by 64 regular longitude/latitude global horizontal Gaussian-grid with a resolution, corresponding to the resolution of 2.8125 x 2.8125 degrees. The vertical layers have a resolution of about 1 km near the tropical tropopause, and a much higher resolution near the surface, the 10 km top layer is centered at 0,11 hPa. But it's also possible to run with higher resolution. Figure 3.1 gives an illustration of the resolution for L60/L40 and T42/T159.

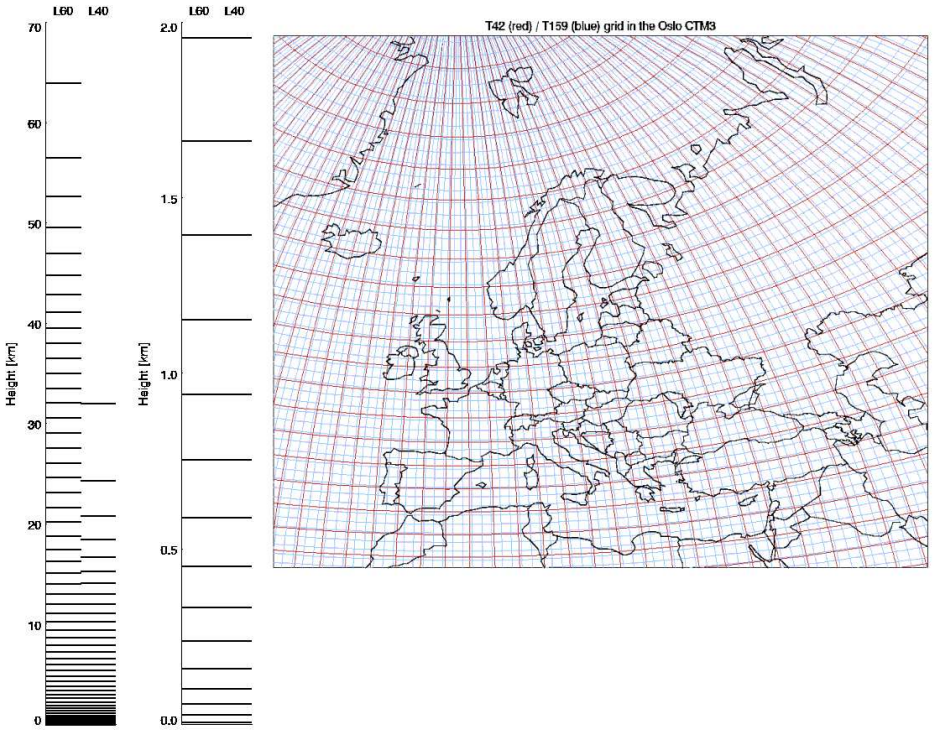

Figure 3.1: Illustration of grid resolution in the Oslo CTM3. To the left: Mean center of layer heights in the Oslo CTM3, for L60 and L40 resolution. Vertical axes are height in km; left: 0-70km, right: 0-2km. To the right: The T42 (red) and T159 (blue) grids in the Oslo CTM3. Both pictures is taken from folk.uio.no/asovde/osloctm3/resolution.html

The model has two separate chemistry schemes, one for the troposphere, and one for the stratosphere, where the tropospheric code is a stand alone and can be used without stratospheric chemistry. When running the model with only the troposphere chemistry, model species that are photo-chemical destroyed in the stratosphere are allowed to decay at a fixed rate, while species with a source i the stratosphere are set to model climatological values at CTM levels a few km above the tropopause. The advantages with this division is computational power, for when you're only interested in the lower troposphere. The tropospheric chemistry is run with 46 species and some intermediate short lived species only treated within the chemistry (local steady state, don't get transported), that with a numerical time step of maximum 15 minutes (expect from OH/HO_2/RO_2-reactions which uses 1/3 of this time) depending on the operator-split time. It is possible to run with different time steps, treating for example chemistry and and transport at different times, the only criteria is that all process sub-cycles sync at the end at the operator-split time step which is usually 60 minutes. All the operations is carried out sequentially and asynchronously. The components included in the tropospheric chemistry is listed in appendix 7.

The model uses three different transport schemes, one for the large-scale advection, one for the convective transport and one for the boundary layer mixing. The large-scale advection uses a

Second Order Moment (SOM) scheme updated in 2006 (*Prather* (1986)), this is highly accurate, and low-diffusive. The convection is described by Tiedke mass flux scheme (*Tiedtke* (1989)), using meteorological data calculating convective mass fluxes. Detrainment and entertainment rates is also taken into account to the updrafts and downdrafts. The boundary layer mixing uses Holtslag K-profile scheme (*Holtslag and Bruijn* (1990)).

There are several available emissions data sets for the surface emission in Oslo CTM3, and you can in general run with any emissions scenario. For emission of chemical species by biomass burning, it is taken from the Global Fires Emissions Database version 3 (GFEDv3). Emission of NO_x from lightning is calculated from convective fluxes provided by meteorological data, the mean global annual source is estimated to be about 5 Tg(N) y^{-1} (*Sovde et al.* (2012)).

The dry deposition to the ground is given as a function of land-use, and the standard for Oslo CTM3 uses five categories: ocean, forest, grass, tundra/dessert and show/ice. It also separate between night and day, and summer and winter. In stable conditions it is possible that the molecules on the top of the layer don't reaches down to be deposited on the ground, Oslo CTM3 compensate for this by reducing the deposition velocity slightly in very stable conditions.

As Oslo CTM3 is an offline model it don't make any changes to the radiative forcing when changing the concentration of for example ozone in the troposphere. So to say something about how this will effect both the radiative forcing, and the surface temperature you either need to use a climate sensitivity model, or you can do your own calculation based on the work of these models. In IPCC fourth assessment (*Denman et al.* (2007)) report they presented simplifies expression to calculate the change in radiative forcing based on the change in concentration including methane. For ozone it estimates net normalized forcing per ozone change in Dobson Unit (DU), this is based on published literature where different models has been used to calculate the change in ozone since pre-industrial time and the accompanying radiative forcing. This don't take into account at what height in the troposphere the change is located.

The Oslo CTM3 model is a updated version of Oslo CTM2, with a cleaner code, improved physical parameterization and increased computational efficiency. It has in general shown to simulate the the transport and chemistry well, but it shows a tendency to overestimate NO_x and OH, it also gives a to slow Brewer-Dobson circulation (*Sovde et al.* (2012)).

3.2 My Settings

I ran the model with the standard resolution T42L60, this is the coarsest of the alternatives giving lower precision when looking at smaller areas, but it is the most computational effective of them. This means that when looking at single point concentration, one needs to take into account that the grid is large, and is most likely affected by local chemistry and meteorology from nearby places. It is especially important to have this in mind when looking at for example rural areas where there is a large city or industrial area nearby, as these two places may lie in the same grid and local effects get diluted out affecting the entire grid.

In this study I'm only looking at the troposphere, and have therefore turned off the stratosphere chemistry. This gives an advantages in computational efficiency, and increases the speed of the model. The transport across across the tropopause is instead set by climatological gradi-

ents, this won't is not important in the lower and middle troposphere, but it can lead to some errors in the upper troposphere. However, this is of less importance when comparing two different simulations.

Because I'm concentrating on ozone, and the chemistry related to this, I chose to run without the Black and organic carbon package. Black carbon deposition in for example the Himalayas may have a large impact on radiative forcing over India, but as this is a off-line model, these changes will not affect my results. Since I'm not planning to look further into this, I chose to run without this module. The same goes for the other extra packages as sea alt, mineral dust, and the nitrate package, I'm not planning to look more closely into any of these compounds, as I'm focusing on gas-phase chemistry. The connection between the aerosol packages, and the gas-phase chemistry is small, but the connection that is will be lost as I'm running without, and this might affect the results, exactly how much is hard to say, but the connection is so small that it can be neglected. I have also turned of the sulphure chemistry, as it's impact on ozone or any of the ozone precursors is so small that it can be left out.

All my runs is started 1.January 2007, running them for three years, not allowing for leap year. For cloud cover treatment I have chosen the default option (LCLDRANA), which selects a random fractional area less than one and the optical depth is calculated from that, this is the cheapest and fastest (*Sovde* (2013)). I also chose the default values for both number of operator split steps per meteorological time step and number of chemical sub steps per operator split step (NROPSM=3 and NRCHEM=1). There is only one boundary layer and dry deposition scheme available at the time, so here I had to use the Prather scheme for the boundary layer and the simple UCI scheme for the dry deposition. I've started all my runs from a reestartfile. For any other possible adjustments not mentioned here I have not made any changes, an used the settings set as default or recommended by the user manual.

The emission scenario I have used is from *Lamarque et al.* (2010), a data set with the primary purpose to be used for creating consistent gridded emissions for the Climate Model Intergovernmental Program #5 (CMIP5) in support of the Intergovernmental Panel on Climate Change (IPCC) Fifth Assessment report (AR5). Testing of the data sets ability to capture long-term changes in ozone, CO and aerosols shows a little to slow long term change in the Northern mid-latitudes surface and mid-troposphere ozone compared to observations, but besides from that the emissions seems to be in good agreement with previous published estimates and observations (*Lamarque et al.* (2010)).

For more information on setup option and how the model works I refer to the User Manual by Ole Amund Sovde.

Chapter 4

Model Validation

To be able to say more about the weaknesses and strengths of the model, I will compare the model to some observations. This can be useful when evaluating my later results, and it will also lend more confident to my results. If for example the model seems to simulate concentrations over the oceans very well, but shows large errors over the continents this is important knowledge when looking at the later model results. I have compared my simulations with both ground based observations, observations made from ozonesonde measurements and satellite. The use of observations from satellite is very valuable, especially over regions with few ground based observations which is the case for India. Figure 4.1 shows the locations of the different ground based stations (pins) and where the ozonesonde measurements (dots) is made.

First I have included two figures (4.2 and 5.4) of the modeled ozone concentration at 0.01 and 0.1 km height (approximately first model and fourth model layer) showing the concentration and spatial distribution of surface ozone. Figure 4.2 shows for winter a clear separation along the coast with higher concentrations over the ocean, in spring the winds changes from off-shore to on-shore (chapter 2, sections 2.2), this dividing gets partially washed out, and the concentrations is almost the same over land as over ocean. In summer the monsoon comes inn, and the concentrations along the coast and over ocean is reduced. During fall the geographical pattern is more similar to winter, and we see a dividing along the coast with higher values over the oceans. The effect of the wind changing from off-shore to on-shore is present in all the seasons. Comparing this to a similar simulation done by WRF-chem shown in figure 2.4 in chapter 2, we see similarities but my simulation gives higher concentration of the ocean and lower values over land. I have also plotted the 0.01 km ozone concentration for the entire world (not included here), and the same pattern with a clear contrast between land and ocean can be seen for almost the entire coastline around the continents.

Figure 5.4 shows a geographical pattern more similar to the one simulated by WRF-Chem in *Kumar et al.* (2012) shown in figure 2.4, with higher values over land in than figure 4.2 shows. Over ocean the concentrations is similar to the plot at 0.01 km, and except for a higher concentrations over land in general, the geographical pattern has several similarities.

Because of this dividing, and the higher concentrations over ocean I suspect that there might be something wrong in the bottom layer of the model at 0.01 km, the plot for 0.1 km shows what seems to be a little to high values, but the geographical pattern is more similar to what we would

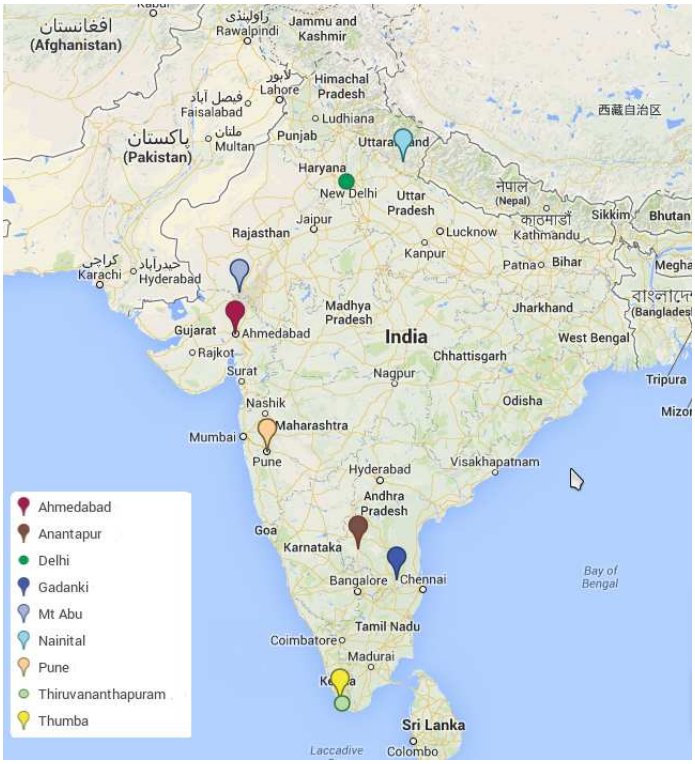

Figure 4.1: Map over India with locations of where the different observations is from. Circles is ozonesonde, and pins are ground observations. The map is made in Google maps.

expect. I will therefor use concentrations from both 0.01 and 0.1 km height when validating.

4.1 Time series and Spatial Distribution

In this section I will validate simulations to ground based observation, plotting the modeled surface values together with the observations as a time series to evaluate the model skill at calculating the concentrations, and to capture seasonal variations. This is done for CO, NO_2 and ozone. I will show figures of the total tropospheric column for CO and NO_2, together with some observations to give a picture of the spatial distribution of the precursors, and compare ozonesonde observations to height profiles. All the observations are taken from (*Kumar et al.* (2012)).

4.1.1 CO

Figure 4.4 shows ground observations of CO at three different sites plotted together with modeled CO at two different heights, 0,01 km to the left, and 0,1 km to the right, which approximately corresponds to level 1 and 4 in the model. CO has a lifetime of about 2 months (*Jacob* (1999)),

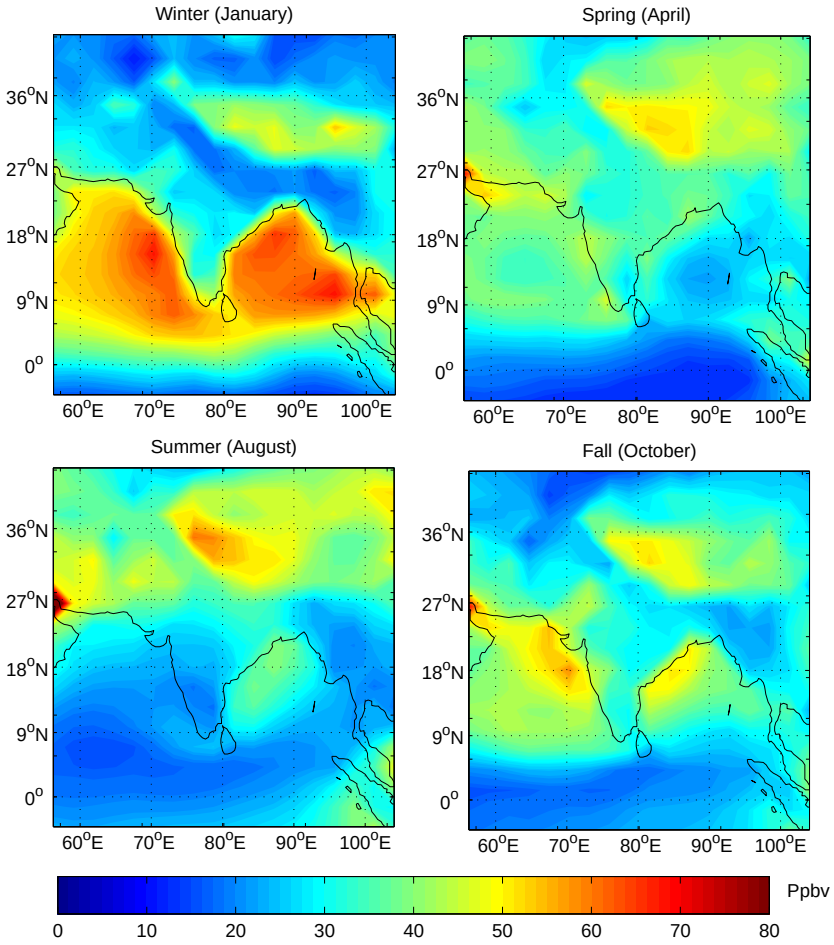

Figure 4.2: Ozone concentrations at 0.01 km height for the four seasons modeled by the Oslo CTM3. Concentrations are shown in ppb.

meaning that it will get well mixed higher up in the troposphere away from the emission source. The modeled concentrations at 0,1 km height is fairly similar for all the different locations indicating that at this height the gas is already mixed and seasonal and local differences in emission gets more wiped out. The modeled concentrations for 0,01 km on the other hand, shows a much larger seasonal variation, especially for the urban location - Ahmedabad, indicating that local emission has a larger impact on the concentration.

For Ahmedabad the simulation at 0,01 km is quite good, and the model reproduce the seasonal variation well, but it don't catches the highest concentrations during winter and underestimates the values during this season. Ahmedabad is a large city, with high local emissions, especially during winter, and with the coarse model grid this will probably get diluted out and the model don't catch these "tops" in concentration.

Mt.Abu is high altitude and located at 1680 m with relatively low local emissions, and the

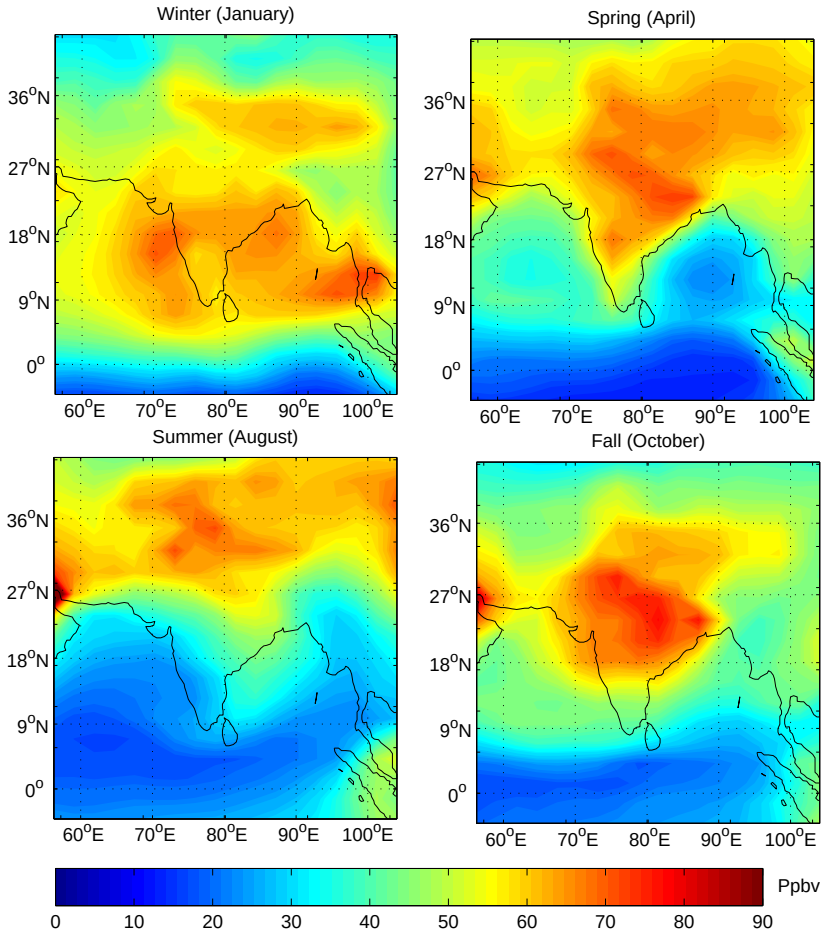

Figure 4.3: Ozone concentrations at 0.11 km height for the four seasons modeled by the Oslo CTM3. Concentrations are shown in ppb.

observations shows a fairly flat profile with small seasonal variations. This matches well with the simulations at 0,1 km height, but the one for 0,01 km is not as good. The simulated profiles for Mt. Abu is almost the exactly same as the one for Ahmedabad, a result of them lying close to each other geographically. This partly explains the error in both the overestimated seasonal variation at Mt. Abu, and the underestimated winter values at Ahmedabad, as the large emissions over Ahmedabad contaminates the concentrations over Mt. Abu, and the other way around.

The simulations over Gdanki is fairly good for both the heights, but the increase in CO during winter is only well simulated at 0,01 km height. This is a rural location, with relatively small emissions, and this explains the flat profile with small seasonal differences.

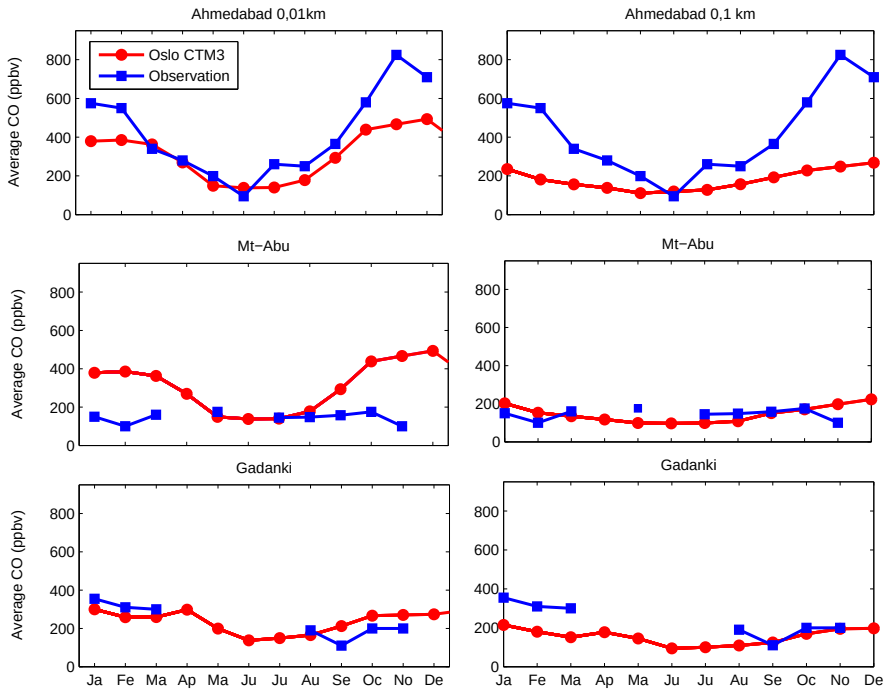

Figure 4.4: Seasonal variation of surface CO modeled with Oslo CTM3 at 0.01 and 0.1 km hight for three chemical different enviroments in India, urban (Ahmedabad), rural (Gdanki), high altitude (Mt-Abu). Plottet together with observations from *Kumar et al.* (2012). Note that the observations is not representativ for the year 2008.

4.1.2 NO_x

In figure 4.5 we see the modeled NO_x concentrations at 0,01 km to the left and 0,1 km to the right, plotted together with ground observations at three different cites. The lower values at 0,1 km is a result of the short lifetime of NO_x (at about a day), and local emission and meteorology plays a bigger part in the concentration. Most of the emitted NO_x at the surface will be destructed before it have the time to rise and spread out. With the coarse grid of Oslo CTM3 these kind of local effects easily get diluted out, and as we saw for CO this is happening in this case as well.

The observations over Ahmedabad shows much higher concentration than any of the other locations, this is to the large local emissions as this is the only large city out of the three. The model has problems simulation the large seasonal variation, but it still catches the pattern with the increased values during winter. At 0.1 km it seems as most of the NO_x is removed and the modeled concentrations is under 2 ppbv, significant lower than at 0.01 km. But as figure 2.2 in chapter 2 show, NO_x concentrations above approximately 0.5-0.8 ppb corresponds to regime 2, so we will still get a net production of ozone.

At both Mt-Abu and Gdanki the model simulation at 0,1 km seems quite good, while the

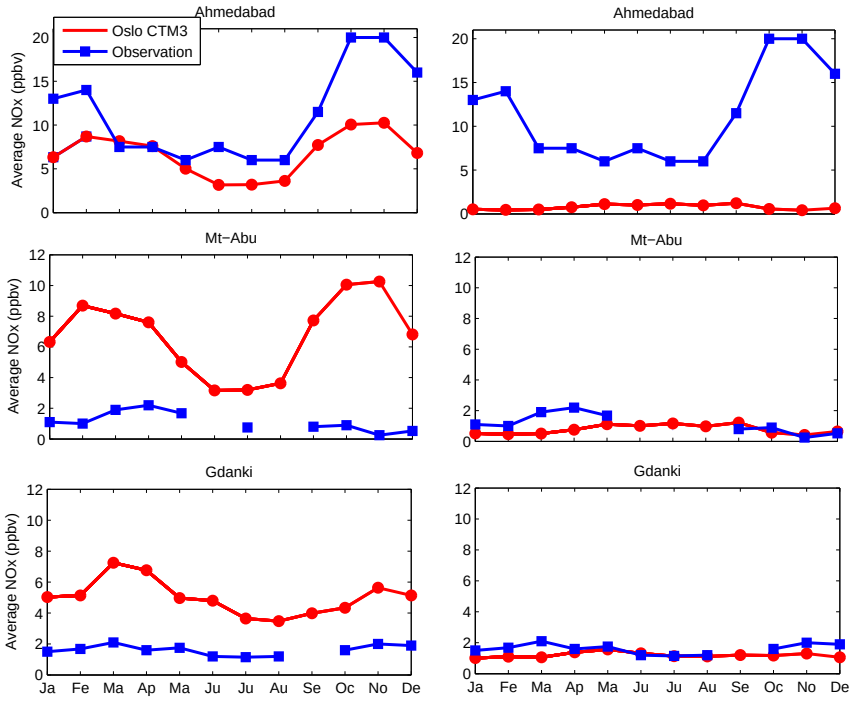

Figure 4.5: Seasonal variation of surface NO_2 modeled with Oslo CTM3 at 0.01 and 0.1 km hight for three chemical different enviroments in India, urban (Ahmedabad), rural (Gdanki), high altitude (Mt-Abu). Plottet together with observations from *Kumar et al.* (2012). Note that the observations is not representativ for the year 2008.

simulation at 0,01 km overestimates. Both Gdanki and Mt-Abu are low emission cites, meaning they both have lower local concentration of NO_x compared to larger cities, and even a relatively small emission source of NO_x within the same grid could give increased modeled values here. For Mt.Abu this is clearly what has happened, as it lies, as discussed before, in the same grid box as Ahmedabad and the simulated NO_x time series is almost identical to each other. The simulated time series over Gdanki lies closer to the observations, but it is still way to high. This is probably also a result of it lying inside the same grid as a larger emission source.

4.1.3 Spatial distribution of CO and NO_x

To get a better picture of the models ability to simulate the spatial distribution of the emissions, I will also compare longitude / latitude plots of the total tropospheric CO and NO_x column with satellite observations. These plots will also illustrate the difference between the different seasons and the spatial distribution of the concentrations, which can be helpful when looking at the ozone production later.

Figure 4.6 shows the tropospheric column concentration for CO for the four different seasons

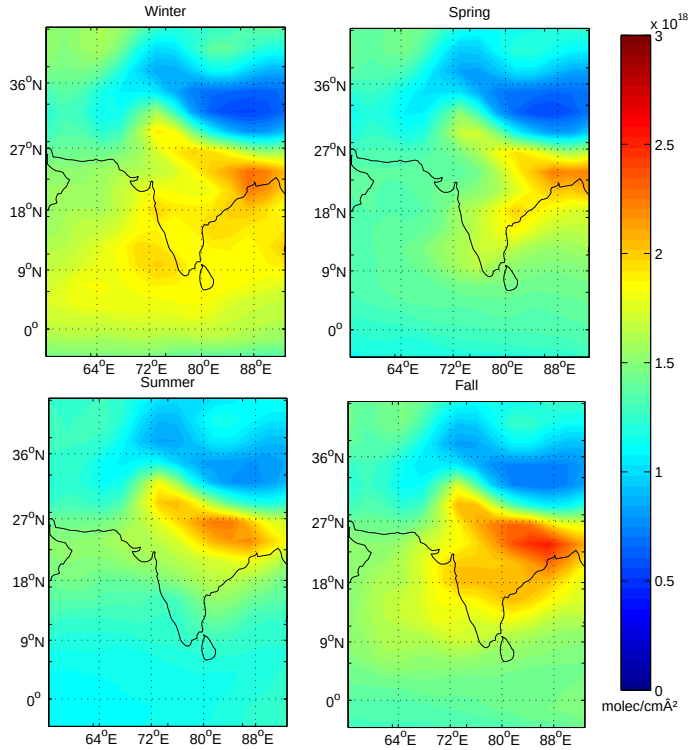

Figure 4.6: Spatial distribution of Oslo CTM3 simulated tropospheric column CO for winter (DJF), Spring (MAM), Summer (JJA) and Fall (SON) for 2008

for 2008, modeled by Oslo CTM3. You can clearly see where we find the IGP as this is an area with high concentrations in all the seasons, just north of the IGP is the Himalayas, an area with lower concentrations. This figure also show the highest CO-concentrations in fall, and the lowest during summer. I will compare this with the left side of figure 4.8, which shows satellite observation from 2008, retrieved by MOPPIT for the four different seasons, it shows the total column, but is mostly representative of free tropospheric CO (*Kumar et al.* (2012)). As the observations is for the entire column, and my figure is only representative for the troposphere, I can't compare them directly, but it will give an idea of weather my model is reasonable or not. The spatial distribution of CO is fairly similar in the two figures, my figure captures the increased CO concentration in east, and the very low values over the Himalayas. It captures the large spread over the oceans in winter, in spring this is slightly underestimated, but it captures the higher values at the east coast. So in general the spatial distribution is quite similar, and so is the concentrations.

On the right side of figure 4.8 is observations of the tropospheric column from satellite, showing the concentration and spatial distribution of NO_2 retrieved by OMI, the plot is taken from *Kumar et al.* (2012). Comparing these observations to figure 4.7, which shows the tropospheric column of NO_2 for the four seasons modeled by Oslo CTM3, shows a rather bad consistency. The model seems in general to overestimate the concentrations, except from over the IGP in

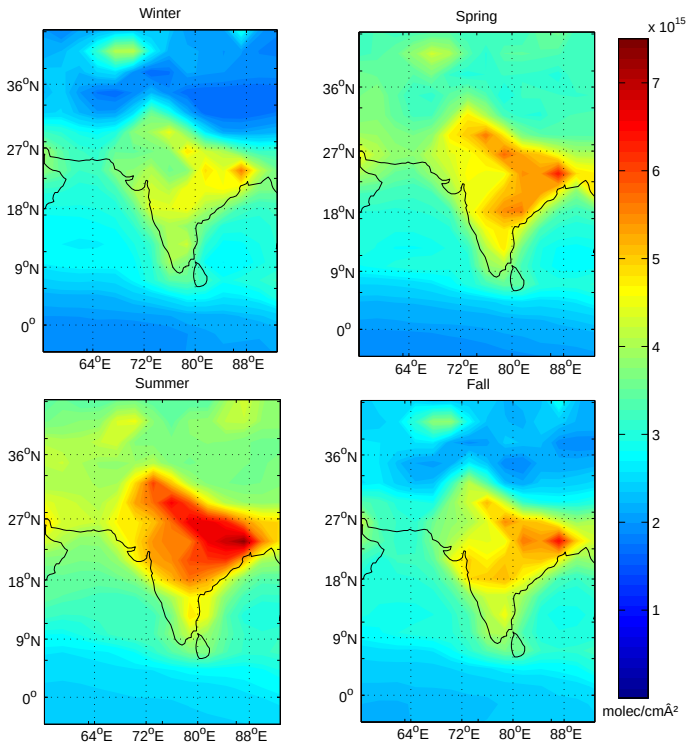

Figure 4.7: Spatial distribution of Oslo CTM3 simulated tropospheric column NO_2 for winter (DJF), Spring (MAM), Summer (JJA) and Fall (SON) for 2008

winter, where it slightly underestimates. However, the geographical pattern with slightly higher concentrations over the IGP, lower concentrations over the west coast under the monsoon, and higher on the east coast for all the seasons expect fall is simulated well by the model. The highest concentrations is in summer according to the model, which is the opposite of what the observations show, meaning the model is heavily overestimating the summer concentrations. For spring the consistency is better, the model is still overestimating, but the concentrations over the IGP is better captured.

These results is consistent with what the time series show, because of the coarse resolution very high local concentrations will be diluted out and give to low values over the larger cities and to high values in the rest of the grid. The observations show a much more "spotted" spatial distribution, with very high values over the larger cities, this is what Oslo CTM3 misses. Another thing that is noteworthy is the inconsistency between at what season the highest and lowest NO_2-concentrations is seen, the model gives the highest during summer, and lowest in winter, while for the observations it's the other way around. Looking at a similar plot for the ground concentrations at 0,01 km height, it shoes higher concentrations in winter than in summer (not shown here), so the problem must lie higher up.

In summer there is more convective mixing transporting pollution at the ground higher up in the troposphere, giving a straighter height profile for NO_2 in summer, while in winter the

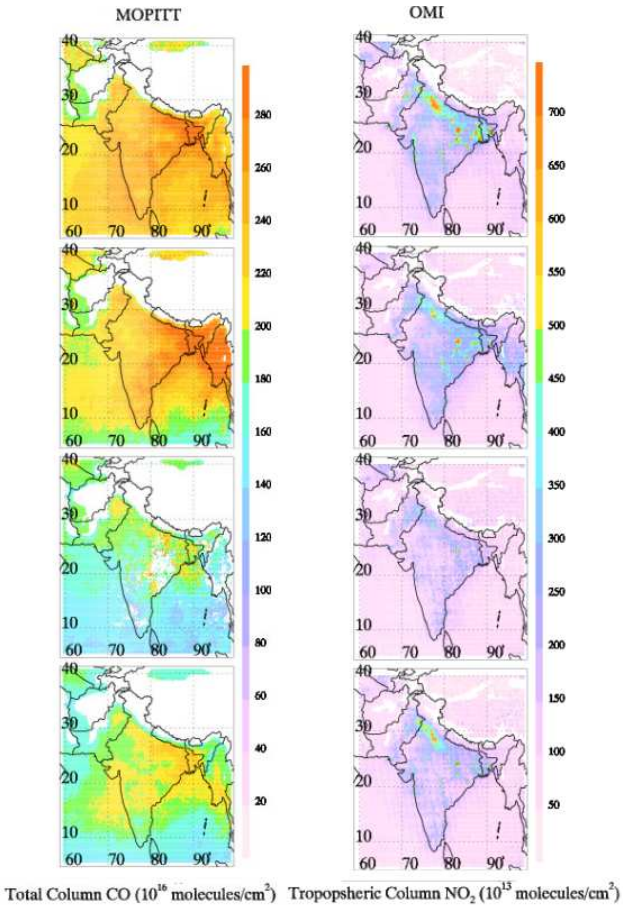

Figure 4.8: Observations of CO and NO_2, retrived by satalites for winter (DJF), Spring (MAM), Summer (JJA) and Fall (SON) for 2008. The CO it shown the total column retrived by Measurments of Pollution in the Troposphere (MOPITT), and tropospheric column retrived by Ozone Monitoring Instrument (OMI). Both figures is taken from *Kumar et al.* (2012)

concentrations faster toward zero. But you would also expect longer lifetime of NO_2 in winter as the solar radiation is lower. Looking at the concentrations the model seems to simulate well in winter, and the problem is the overestimating in summer. Since the reason for the higher column concentration seems to lie higher up in the troposphere, it could be that the transport across the tropopause is to large, or that it transports NO_2 to far down into the troposphere during summer. Another possibility is lightning, in summer the convection is stronger and more lightning, but it could a to high production of NO_x from lightning that is the reason for the high concentrations.

4.1.4 Ozone

Figure 4.9 and 4.10 shows seasonal variations of the ozone concentration, and compares observations from ground stations with monthly averaged modeled ozone concentration at 0.1 and 0.01

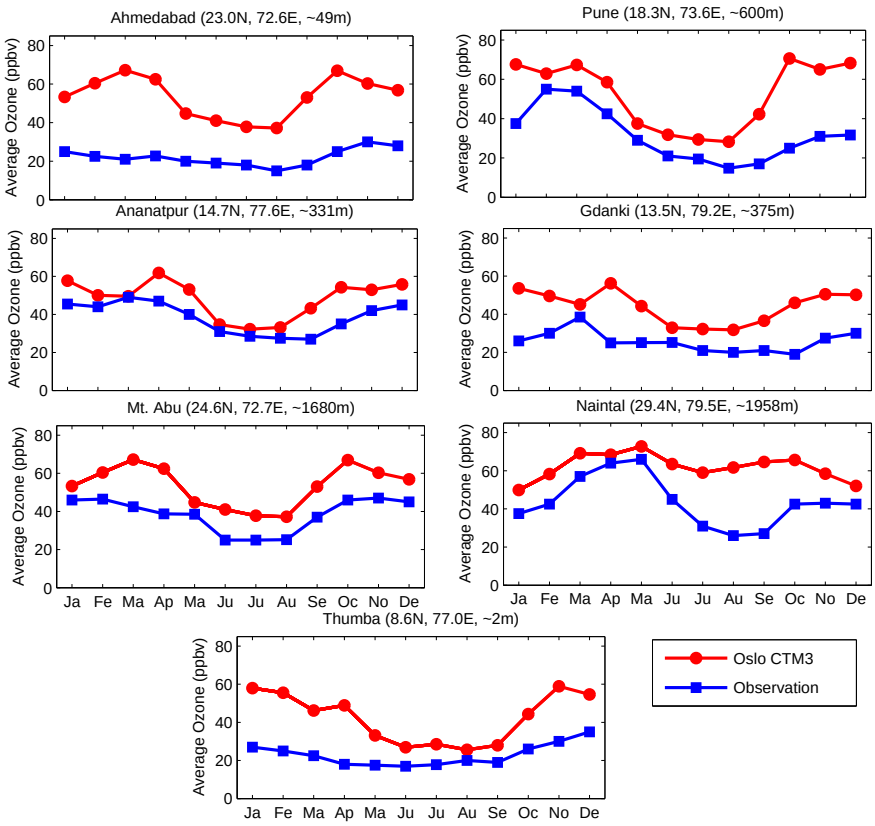

Figure 4.9: Seasonal variation of surface ozone modeled with Oslo CTM3 at 0.1 km hight for four chemical different enviroments in India, urban (Ahmedabad), semi urban (Pune), rural (Ananatpur and Gdanki), high altitude (Mt-Abu and Naintal) and costal (Thumba). Plottet together with observations from *Kumar et al.* (2012). Note that the observations is not representativ for the year 2008, expect from Naintal.

km height. This is done for seven different locations located within the Indian region, representing different five regions - rural (Ananatpur and Gdanki), high altitude (Mt. Abu and Naintal), urban (Ahmedabad), semi urban (Pune) and marine (Thumba).

In figure 4.9 the model over estimates the ozone concentration slightly in all the locations, in Ahmedabad which is the only urban location of the seven, the model overestimates more. In general it seems to capture the seasonal variation well at all the different cites. The model simulation at 0.01 km shown in figure 4.10 give a slightly better picture, and for all locations except Naintal the simulations lies closer to the observations and captures the seasonal variations well.

In the rural (Anatatpur and Gdanki), and high altitude (Mt-Abu and Naintal) locations the anthropogenic emissions are low compared to the bigger cities and other more populated cites. Here the model underestimates the concentrations at 0.01 km slightly (figure 4.10), this is especially true for winter, and in general the simulations gives a more flat profile than the observations

show for these four locations.

Ahmedabad is the 5th biggest city in India, with large emissions of CO and NO_x, this means that we probably will get NO_x-titration at the surface (chapter 2, section 2.1.1), reducing the ozone concentration, giving lower ground concentrations in the city than over less polluted areas. It also lies close to Mt.Abu, a high altitude location with less pollution and cleaner air. As these two locations lies close, the model result is almost the same, while the observations is quite different because of the large difference in local emissions.

The modeled concentrations at 0.1 km (figure 4.9) largely overestimates the ozone concentration over Ahmedabad, while the concentrations at 0.01 km (figure 4.10) parts by less than 10 ppbv, and captures the low ozone concentration by NO_x-titration well. For high altitude Mt. Abu it's the other way around, with a better match with the 0.1 km model run. This could either be because the model overestimates the ozone production, and there is a problem in the bottom layer reducing the concentration, creating what seems like a good result over Ahmedabad, and underestimates the concentrations over Mt. Abu. Or the emissions over Ahmedabad is large enough to titrate out ozone in the entire grid when diluted out by the coarse resolution, giving good results over the city, and too low concentrations over less polluted areas like Mt. Abu.

Over the city of Pune the model capture the ozone concentration well, both at 0,1 and 0,01 km. We get a maximum during late winter/spring, as a result of the concentrations of NO_x and CO being at its maximum during winter (figure 4.8, section 4.1.3), and the increase in incoming solar radiation during the transition from winter to spring. The model result at 0.01 km height, is slightly better than for 0.1 km, especially for the spring concentrations.

Ananatpur and Gdanki are both rural areas with relatively low emissions of both NO_x and CO (KILDE), they both lie south in Asia, but Gdanki lies closer to the coast. The model results for the two stations are almost the same (probably because of the close locations), but the ground observations at Ananatpur shows slightly more seasonal variation than Gdanki. Over Gdanki we get more marine air with low ozone concentrations blowing in from the coast, reducing the ozone concentration and flattening out the profile. Simulations at both height captures the seasonal variation fairly good, the simulation at 0,1 km is a little better for Anantapur, but for Gdanki the simulation at 0,01 km height is the best.

Naintal is located at 1958 meter in the Himalayas, here the topography is complex with height differences by about 2000m over distances less than 50 km. This makes it difficult to model the ground concentrations, with the coarse model grid. Here the 0.01 km run is no good, and we cant say that the results here can be trusted, the run at 0.1 km i better, and capture the seasonal pattern to some extent. A higher resolution would probably give better results, but I have no findings supporting that.

Thumba is a village near the south coast, with large influence from marine air, blowing in from the ocean. This gives low ozone concentrations, and small seasonal variations. At both heights the ozone concentrations is overestimated, indicating either an overestimation of the emissions, or an underestimation of the influence from the marine air masses. A height profile of the ozone concentration here (not included) shows small differences in the ozone concentration with height, explaining the small difference between the different results, and also indicates that the column is well mixed.

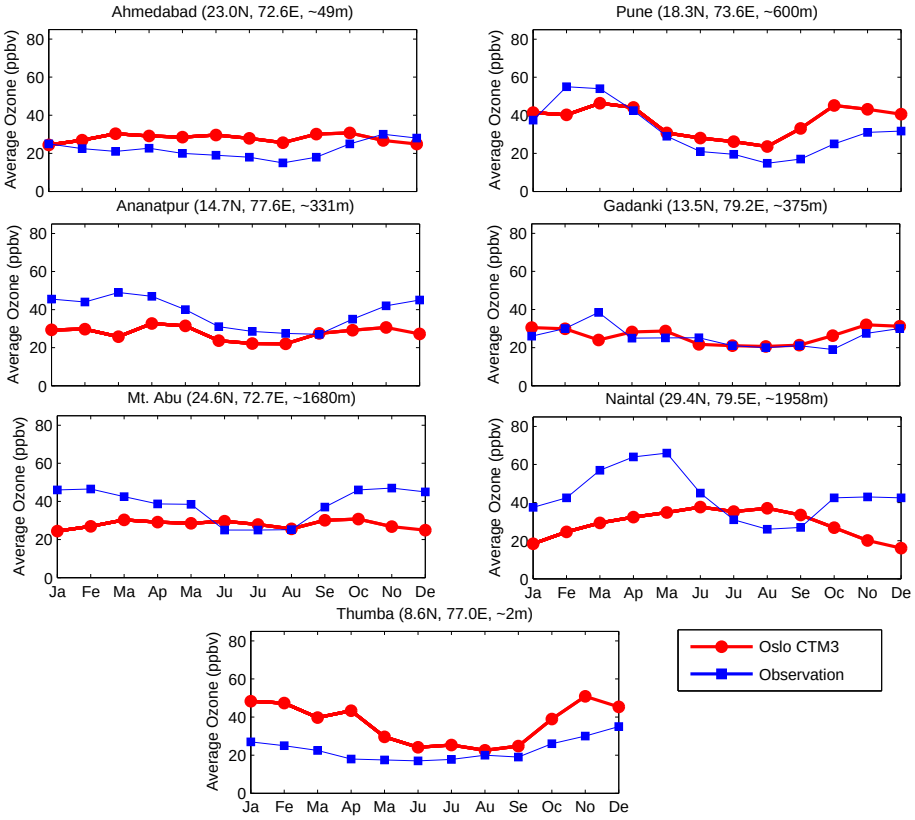

Figure 4.10: Seasonal variation of surface ozone modeled with Oslo CTM3 at 0.01 km hight for four chemical different enviroments in India, urban (Ahmedabad), semi urban (Pune), rural (Ananatpur and Gdanki), high altitude (Mt-Abu and Naintal) and costal (Thumba). Plottet together with observations from *Kumar et al.* (2012). Note that the observations is not representativ for the year 2008, expect from Naintal.

4.1.5 Discussion

This odd division between ocean and land ozone concentrations seen in figure 4.2, together with the inconsistency between the ozone concentrations from the figure presented by *Kumar et al.* (2012) in the theory chapter (chapter 2) and my model, made me think that there might be a weakness in the bottom layer. This could either be a weakness with the models dry deposition or the exchange with the level above because of a to thin level compared to the time step. The time series plot at 0.01 km (figure 4.10) however, shows a good consistency between the observation an med modeled values at 0.01 km for all the locations except Naintal (high altitude). The model seems to capture the NO_x-titration effect (chapter 2, section 2.1) over the urban locations, and catches the seasonal variations well. The timer series plot at 0.1 km (figure 4.9) overestimates the concentrations slightly at all the locations.

What I thought was a weakness might also be a result of the coarse resolution, if for exam-

Location	Observed Value	Modeled Value	Error
Bay of Bengal 1 (10N 86E)	19 ppbv	30 ppbv	+ 11 ppbv
Bay of Bengal 2 (15N 84E)	25 ppbv	38 ppbv	+ 13 ppbv
Arabian Sea 1 (12N 62E)	28 ppbv	38 ppbv	+ 10 ppbv
Arabian Sea 2 (16N 66E)	20 ppbv	28 ppbv	+ 8 ppbv

Table 4.1: Observed and modeled values for two locations in the Bay of Bengal and the Arabian Sea and the difference between them. The observed values is taken from the presented results from a research vessel *Srivastava et al.* (2012), and represent observation for one day at one specific point, the modeled values is the average for the month the observation is from at the same point.

ple a high emission source lies within the same grid as the rural observation point, the diluted emission could be large enough to create a NO_x titration effect in the entire grid. To try and get a better picture of where the weakness lies, I've compared the lowermost values with some observations done over both the Arabian Sea, and the Bay of Bengal.

There is not as many observations over the ocean as over the continents, but during spring 2006 the research vessel Sagar Kanya did measurements of both O3 and CO over the Bay of Bengal and the Arabian sea (*Srivastava et al.* (2012)). Comparing observations made at one single point for one single day, to monthly means will in combination with the fact that these observations is from 2006, and my model run is using 2008 meteorology gives room for large uncertainty's. Still it gives an indication on how well my model simulates surface ozone over ocean. Also, when you only got one observation at each locations, local perturbation could easily disturb this observation and give a wrongful impression of the concentrations. To give more robust observations, it could be helpful with more measurements taken at each location, and over a longer period of time.

I have compared two locations in the Bay of Bengal and two in the Arabian sea to the surface concentrations of ozone simulated by Oslo CTM3, all the locations I picked is a way of the coast. Table 4.1 shows the results, and for all the ozone values my model gives values about 10 ppbv higher than the observations, meaning it overestimates the ground ozone values over ocean. All observations is taken from *Srivastava et al.* (2012). Other research campaigns that's been done over the Arabian Sea reported ozone concentrations as high as 50-60 ppb close to the shore, and around 40 ppbv further out (*Lal and Lawrence* (2001) and *Naja et al.* (2004)).

It could be that the model overestimates the concentrations over the ocean, while it underestimates slightly over land, if this is the case that could explain the dividing along the coast. But it's hard to say anything for sure, to do that more observations is needed.

Based on these validation I would say that the Oslo CTM3 model simulates ground values fairly good, and give a good overall picture of the pollution situation that could be trusted. When looking at components with short lifetimes as for example NO_x, one really need to take into account how the concentrations will get diluted out, and looking at local values the model cant be trusted. Still, as this model is global and run with a fairly coarse grid, local ground concentration

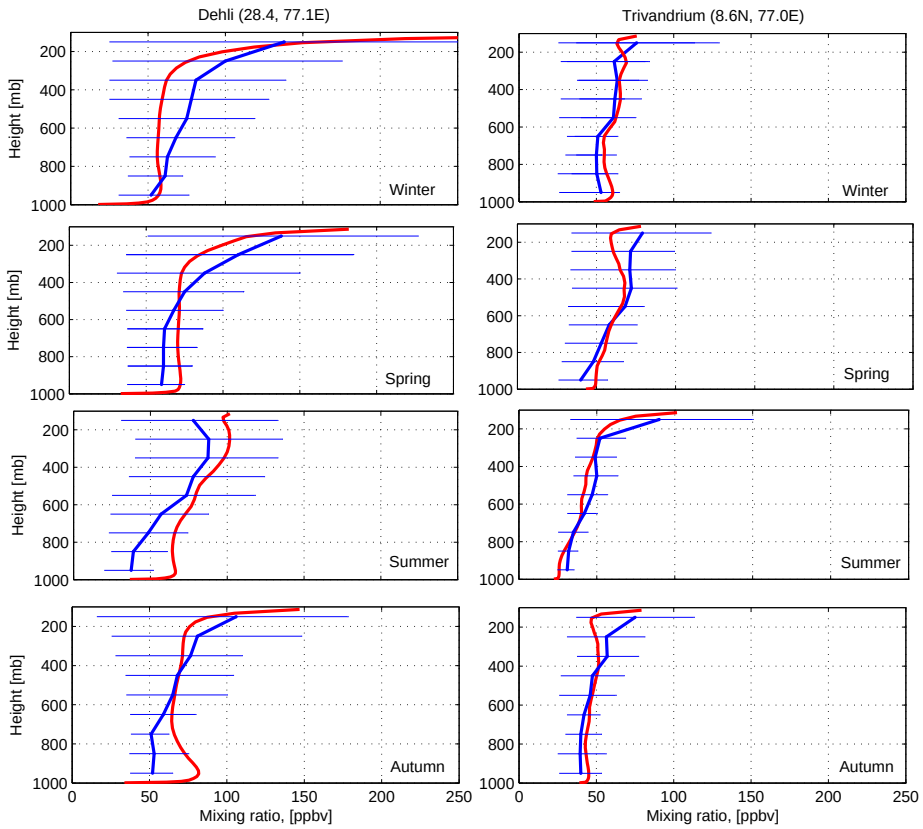

Figure 4.11: Height profiles for the four different seasons of the modeled Ozone concentration over Dehli and Trivandrium plottet together with observations. KILDE OBERSERVASJONER

isn't it's strength, and other models may be more suitable when looking at local pollution at the ground.

As a result of these evaluations I will when evaluating ground concentrations of O_3, CO and NO_x later only include concentrations at 0,01 km height for CO and NO_x, while for O_3 I will sometimes also include results 0,1 km to give a better and more full picture of the ozone concentrations at the ground.

4.2 Height Profiles

Figure 4.11 shows the height profiles for two locations, for the different seasons. This is of importance for the climate, and when evaluating the effect ozone has on the radiative forcing. As discussed in the theory chapter, the ozone located between 7-20 km has a much larger effect on the surface temperature than ozone at the surface has. Delhi is a big city located in the middle of the Indio Gagnetic Plain, and is also one of the most polluted cities in India. Triviandrium is also a city, but its located near the coast south in India, and is therefor largely affected by

marine air masses blowing in from the ocean. The observations is ozonesonde measurements from 2000-2009, and a average over 104 (Delhi) and 103 (Trivandrium) profiles averaged over 100 hPa pressure intervals. The uncertainty represent one standard deviation, meaning 68,1% of the observations fall within the horizontal line.

The model simulates the ozone well over Trivandrium, but over Delhi it underestimates in winter, and overestimates in summer. The model results stays within one standard deviation at all times, expect from in the lower troposphere in summer and fall over Delhi. Here the model overestimates the ozone concentrations with more than 25 ppbv. The reason for the large deviation may be because the emissions is overestimated, or a result of the large grid, and influence from other emission sources or meteorological features nearby. It looks like the model catches the NO_x titration of ozone, as the concentrations near the ground gets really low near the surface. This is especially clear over Delhi, where the emissions is really high. For both cites and all the seasons except for summer over Delhi the model seems to underestimate the ozone concentration in upper troposphere, this might be because the model transports to little ozone down from the troposphere. These values is set by a climatological mean, as I run the model without stratosphere chemistry, and from these plots it seems as this value to low.

Chapter 5

Impacts of Increased Emissions

I have perturbed the anthropogenic emissions of NO_x, CO and the different VOC gasses to a worst case scenario for 2050 using on of the IPCC estimated emission scenarios (*Nakicenovic et al.* (2000)). I chose the scenario family called A1F1, this scenario predict very rapid economic growth, with a fossil intensive technological emphasis, it also include a rapid introduction to new and more efficient technologies. The IPCC report consist of together 40 different scenarios within the four different families, created by six different modeling teams. The future emission prediction I have chosen to use is a mean of the different scenarios within the scenario family, A1F1, in other words its just a rough estimate.

Since the emissions used in Oslo CTM3 is not exactly the same as those the IPCC report uses for 2008, I have estimated how much the increase is from 2008-2050, and increased my emissions by the same amount, meaning a 150% increase in NO_x emissions, and 140% increase in CO and VOC emissions (*Nakicenovic et al.* (2000)).

In this chapter I will look at how this affects the ground ozone concentration. I will also evaluate if a increase in anthropogenic emissions could affect the radiative forcing and surface temperature as a result of a potential increase in ozone in the free troposphere, and a potential change in CH_4 lifetime as a result of changed OH concentrations.

5.1 Change in Surface Concentrations

Figure 5.1 and 5.2 shows the absolute difference in NO_2 and CO concentrations between the model run with 2008-emissions, and the one with perturbed emissions representing 2050. It shows that the largest increase is seen over the IGP where we also find the largest concentrations in general (figure 4.7). The increase is largest in winter and fall which fits well with what we know about when the concentrations in general is the largest (figure 4.8 in chapter 4). These two figures shows the concentrations at 0.01 km height, the same plots for 0.1 km height (not included here) shows a more evenly distributed pattern for both CO and NO_2. But because of the short lifetime the change in concentrations is much lower for NO_2, as discussed in chapter 4, section 4.1.1 and 4.1.2.

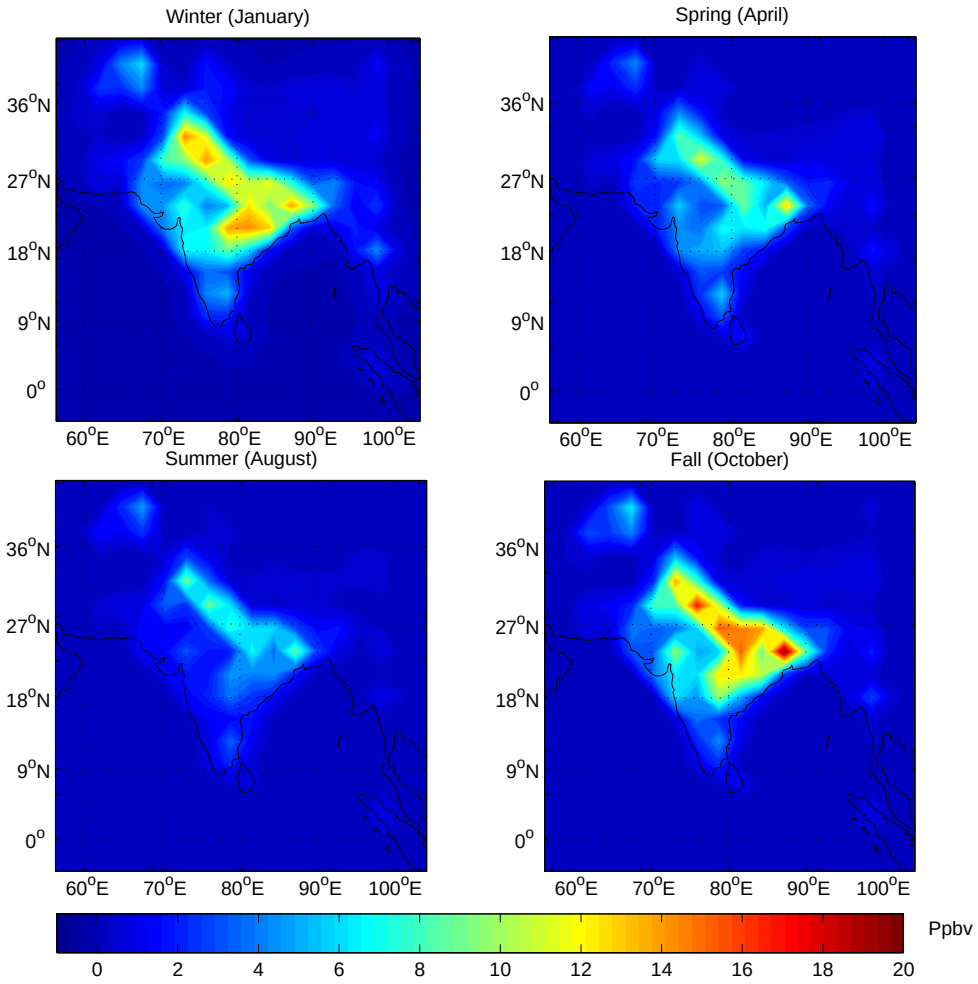

Figure 5.1: Absolute difference in NO2 concentration in ppbv for the different seasons at 0.01km height.

In chapter 2, section 2.1 we saw that when the concentration of NO_x gets high enough it leads to termination of free radicals through reaction 2.13, reducing the concentration of OH. This could lead to an increase in the lifetime of NO_2, and by that give an additional increase in NO_2 concentration. I therefor looked at the relative change in NO_2 surface concentration, to see if there where any non-linear increase in the concentrations. I found a relatively even increase of about 140% over the continent, this is consistent with the increase in emissions. I therefor concluded that this is not the case, and the increase in NO_2 that is seen comes mainly from this increase in emissions.

The increase in anthropogenic emissions of CO, NO_x and VOC's leads to a change in the ozone concentration at 0,01 km between -10 and 50 % depending on season and location, this means a increase of up to 35 ppbv at some locations. Figure 5.3 shows the simulated ozone concentration at 0.01 km height for the four different seasons with emissions representing the

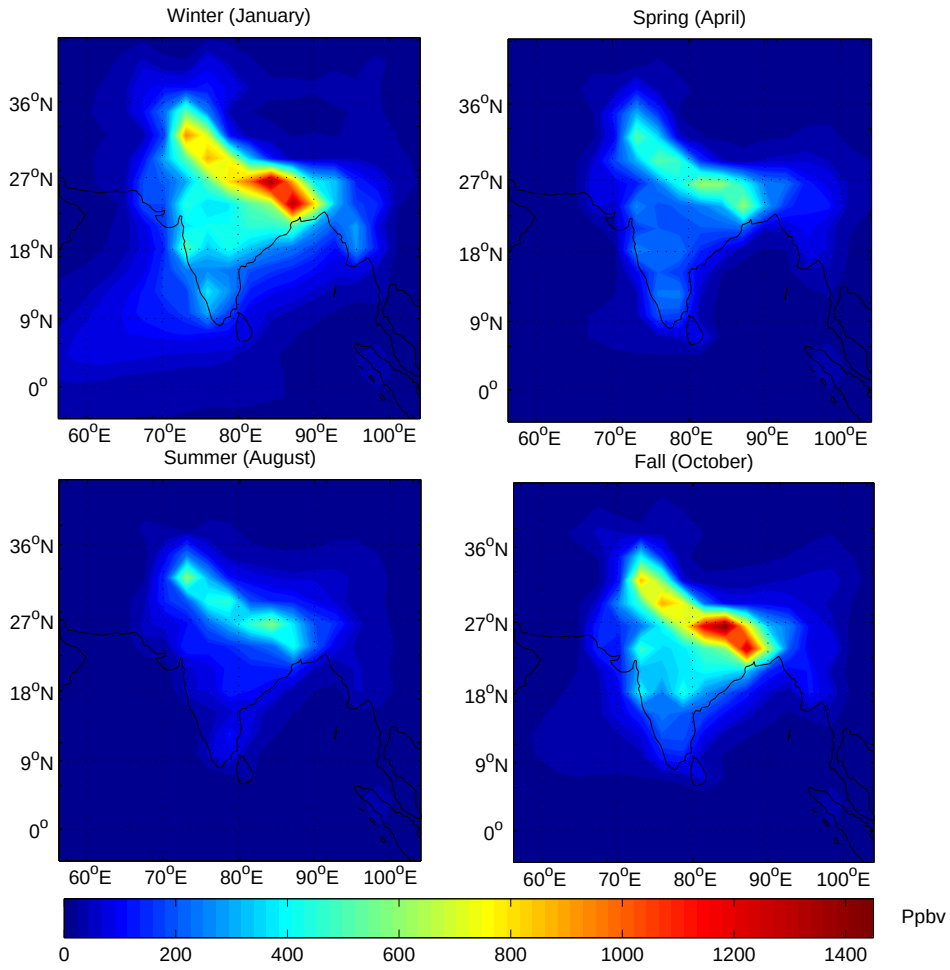

Figure 5.2: Absolute difference in CO_2 concentration in ppbv for the different seasons at 0.01km height.

year 2050. The geographical pattern of where you find the highest ozone values are similar to that for 2008, meaning that the largest increase is located where the concentration already is high. Right out side the west coast you see values at 100 ppbv in winter, and also over land the values lies around 50-70 ppbv. The locations with small changes or a decrease in ozone concentration is mainly over the oceans and over the continent further north, but also during the monsoon season the increase in emission don't lead to a very high increase in ozone.

Looking at the ozone concentrations at 0.1 km shown in figure 5.4, the ozone is both more evenly distributed and the concentrations are higher, the geographical pattern is still similar to the 2008 concentrations. The largest difference is that the IGP pops out more clearly in all the seasons except winter, with the highest values over this region. This is as seen in both figure 5.1 and 5.2 the region with the largest increase ozone precursor concentrations. As seen in chapter 4, the ozone values at the bottom level gets reduced because of NO_x-titration (chapter 2). This

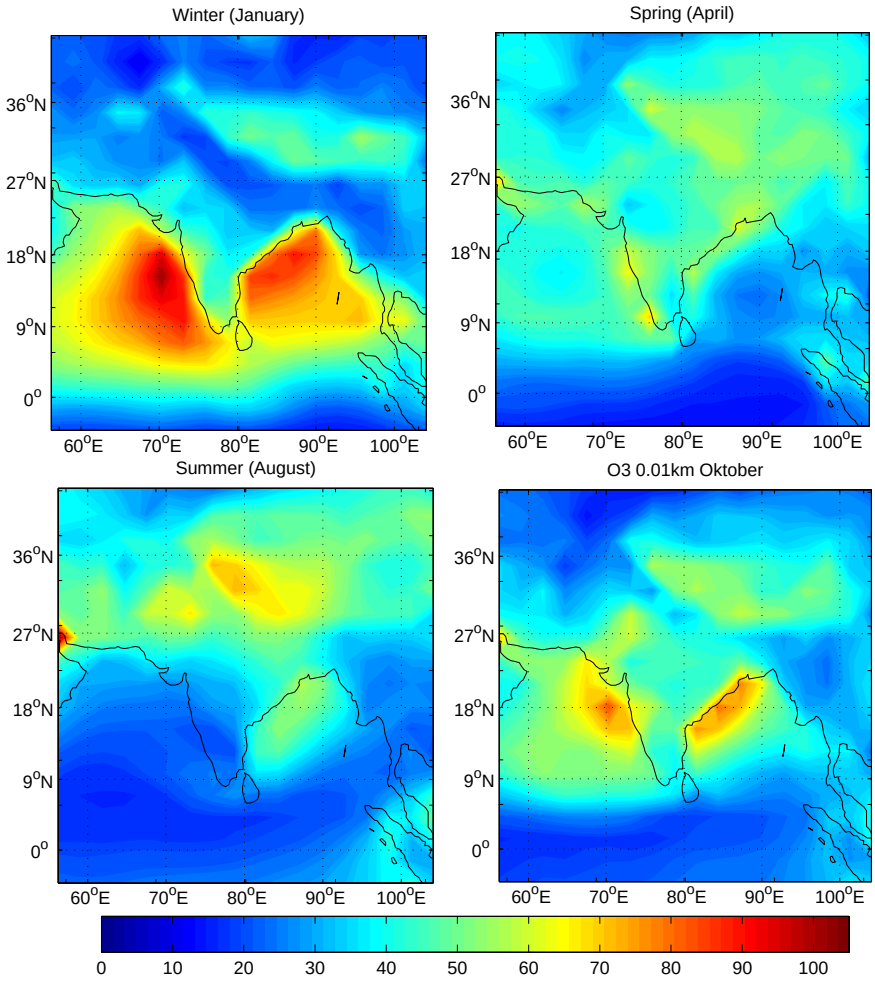

Figure 5.3: Ozone concentrations uising estimated emissions for 2050 in ppbv for the different seasons at 0.01 km height.

effect disappears further up as the concentration of both CO and NO_2 is reduced, leading to an increase in the ozone production. Further away from the emission source pollution will get diluted out as a result of both vertical and horizontal mixing, meaning the pollution spreads out, how far depends on the chemical lifetime and the meteorology.

5.2 Radiative Forcing

Ozone also works as a greenhouse gas, and absorbs short wave radiation contributing to heating of the troposphere. As seen in the previous chapter increased anthropocentric emissions leads to a increase in the ozone concentration at the ground. We also saw that this increase can be dangerous for both human health and vegetation, but to see if this increase has an effect on

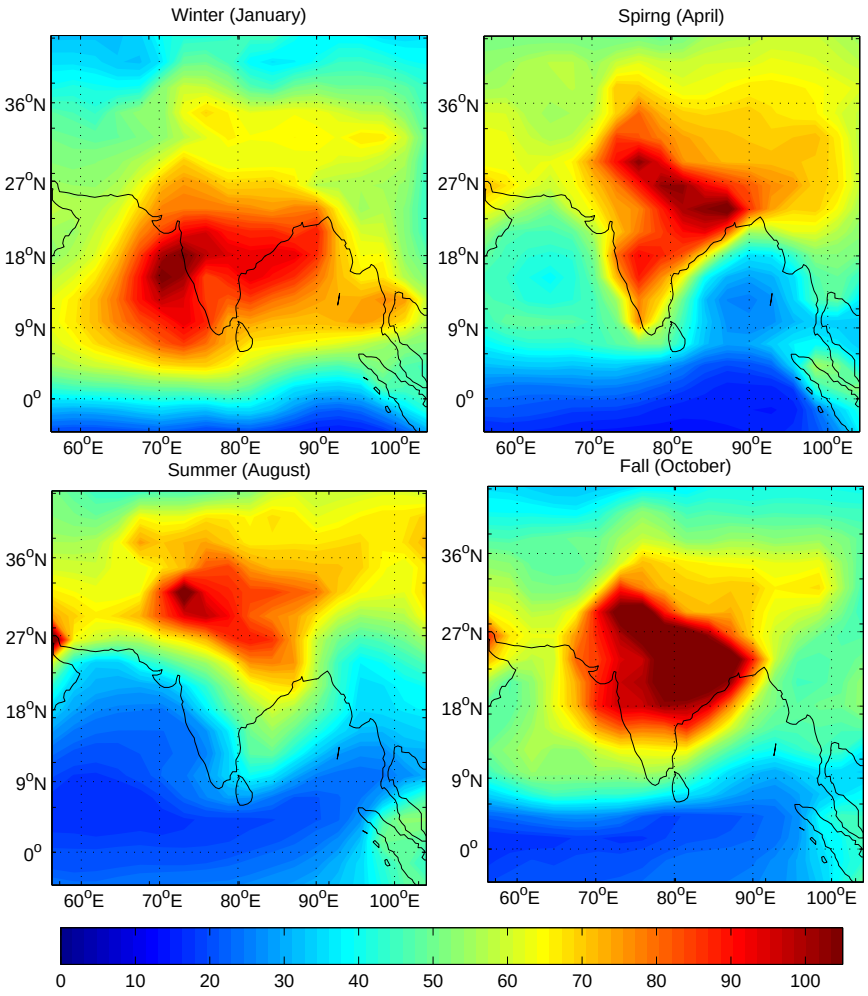

Figure 5.4: Ozone concentrations uising estimated emissions for 2050 in ppbv for the different seasons at 0.1 km height.

radiative forcing it is necessary to look at the vertical distribution. Another question that needs to be answered is whether the large increase in pollution over India will effect the climate outside of India's borders.

A increase in ozone has a larger effect on the radiative forcing higher up in the troposphere, than it does further down (*de F. Forster and Shine* (1997)). So if the increase in ozone at the ground don't get transported further up in the troposphere, or don't affect the ozone concentration higher up in the troposphere, there will be no change in radiative transfer, and a potential change in temperature at the surface can be neglected.

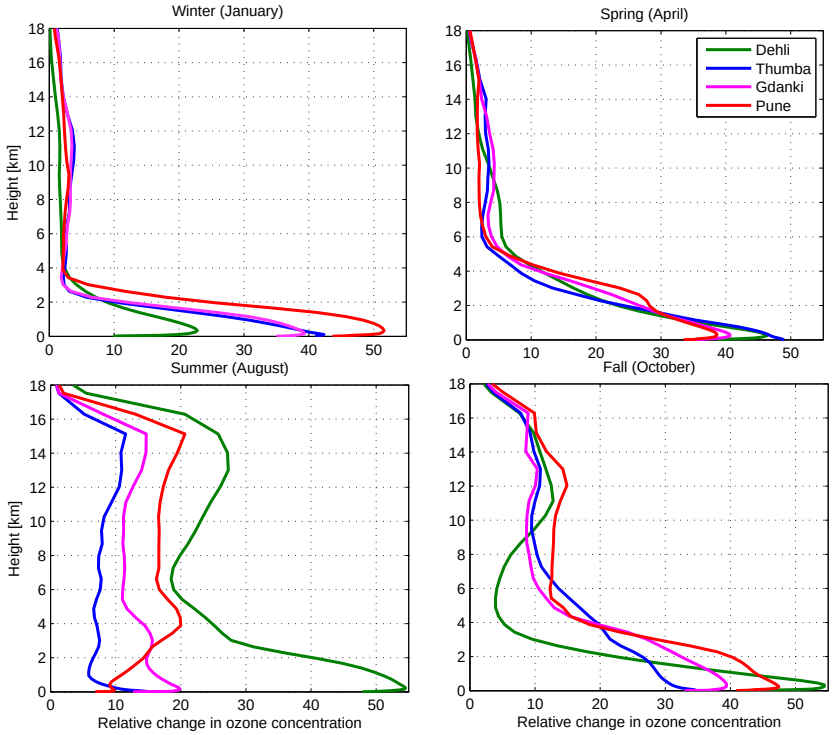

Figure 5.5: Relative difference in ozone between emissions reperesenting 2008 and 2050 for four different seasons and locations in India. Urban and semi urban (Dehli and Thumba), rural (Gadanki) and marine (Thumba).

5.2.1 Height Profiles Over India

Figure 5.5 shows the relative difference in ozone between the model run representing 2008, and the one with perturbed emissions representing the year 2050. It shows four profiles representing different locations and environments, for each seasons. In this section I will focus on the middle to upper troposphere, as the change in surface concentrations where evaluated in the previous section.

Common for all the figures is that the differences between the vertical profiles is larger down close to the ground, and smaller higher up. Meaning it's getting better mixed higher up, while down at the surface emissions and local meteorological features is more important. This is not surprising as it's the anthropocentric emissions at the ground which is perturbed, and it's therefore here the change in pollution will be the largest. The changes down at the surface shows the same overall pattern as we saw in chapter 5, with very small changes down south in summer, and larger differences depending on location for the other seasons.

In winter the absolute increase in ozone concentration is largest close to the surface and reaches a maximum for all locations before 2 km. The increase stays relatively large in the boundary layer, but at around 2,5 km all the profiles goes toward 2-4%. The reason for this is

that it's less convective mixing in winter, and at these stations the increase in pollution down at the surface don't get mixed higher up, giving a increase in ozone in the middle and upper troposphere close to zero. The increase at the surface shows the similar pattern as figure 5.3, and the relative increase in the boundary layer reflects good upon these surface values. Giving a smaller increase over Delhi, and bigger over Pune.

During spring the incoming solar radiation increases and we get a deeper convective mixing, leading to a larger increase in ozone higher up. The different profiles shows a increase between 10 and 20% at 3,5 km, while at the 6 km level the spread is reduced to 5%, meaning that it's around this level local features looses it's importance.

When summer arrives, so does the monsoon, this means that we get a change in wind patterns and deep convection over land. You clearly see the effect of the monsoon for the three southerly lying locations, here the change in ozone concentration at the surface is smaller than for the other seasons, while for Delhi we see a much higher concentration indicating less influence from the monsoon. But as a result of the deep convection the increase in pollution at the surface get mixed higher up, all the way up to the tropopause. The spread between the different profile stays relatively constant throughout the troposphere, indicating that local meteorological features now plays a role much further up than for the other seasons.

For fall we also see signs of deep convection, the monsoon season is over and the incoming solar radiation is at its maximum, and the increase in surface ozone is larger than during summer. This gives a large increase in surface ozone for all the profiles, and a general increase in 10% in the middle and upper troposphere. The profile for Delhi stands out with a smaller increase around 2-7 km.

Common for all the seasons except summer is that the differences between the locations is reduced higher up, and the difference in increased surface concentrations get erased as the air gets better mixed higher up. This indicates that in the middle and upper troposphere, local meteorology and pollution plays a smaller part than it does closer to the surface. Still we see a general relative increase in ozone in the middle to upper troposphere, sometimes as high as 25%. This indicates that an increase in emissions of ozone precursors at the surface has an effect higher up, it will affect the radiative forcing over the area where the emissions is increased, and lead to a increase in surface temperature. This is especially true for summer and fall.

To say more about how this increase in emissions and ozone concentrations higher up in the troposphere affect the total global radiative forcing I need to look outside of India's borders.

5.2.2 Vertical Section

The general large scale atmospheric circulation consist of air rising around the equator, before its getting transported toward the poles. This means that air rising on the northern hemisphere most often travels to the north pole, and air rising on the southern hemisphere travels to the south pole, as a result of this the exchange of air across equator is slow. India lies on the northern hemisphere, and it's therefor expected that the ozone rising from the surface here will travel towards the northern hemisphere, and this is where we will expect to see the largest potential increase in surface temperature as a result of more ozone.

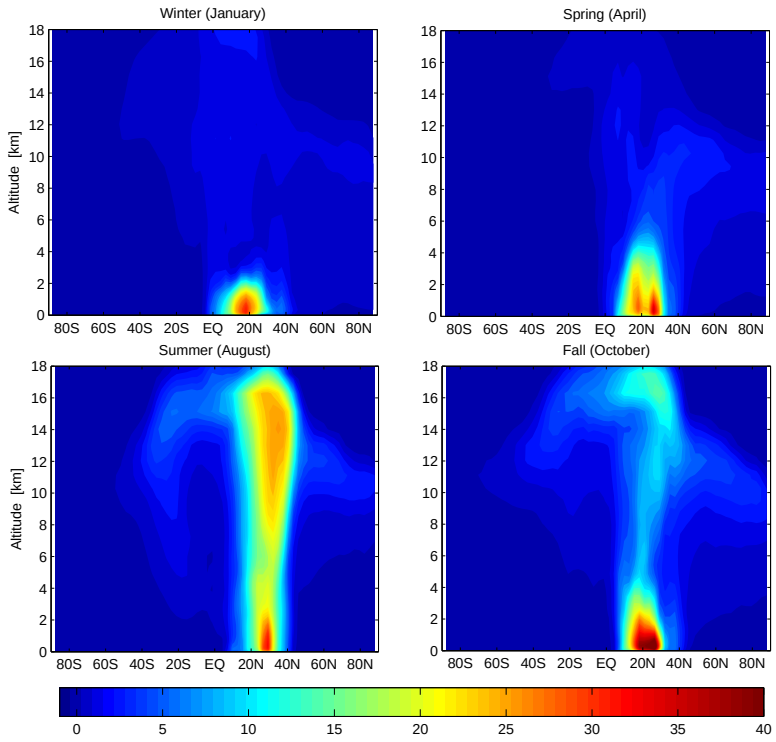

Figure 5.6: Relative change in ozone concentration between emissions reperesenting 2008 and 2050 for the different seasons, plottet as a vertical section at 80 degrees east.

Figure 5.6 shows the relative change in ozone concentration as a function of altitude and latitude. It shows a vertical cut trough 80 degrees east, straight through India. In all the plots it's easy to see where India is located, around 20 degrees north as this is where the emissions is increased and we see a clear rise in ozone concentration.

The local features around India is the same as we saw in the previews section(5.2.1), with a shallow boundary layer during winter, resulting in a increase in ozone close to zero higher up. Still we see a small increase by about 5 ppbv up to the troposphere, and with a small spread, mostly to the north. In spring we also see a quite strong boundary layer, but its not as shallow as the one during winter. The spread of ozone outside this boundary layer shows a similar pattern as for winter with a small increase by about 5 ppbv over the northern hemisphere. Summer and fall shows a different picture with a large column of increased ozone values all the way up the the tropopause. The increase in ozone outside this column is a little larger than for winter and spring, but in summer there is almost no spread toward the north. Only a small increase by about 5% stretching out to 40 degrees south at around 14 km height. For fall we see a similar increase towards the southern hemisphere, but we also get a general spread to the north with a increase at about 2% between 4 and 10 km.

There is two maximum in the relative increase in ozone concentrations, the first one close to the surface, and a second one in the upper troposphere. The first one is self explaining, as it is the

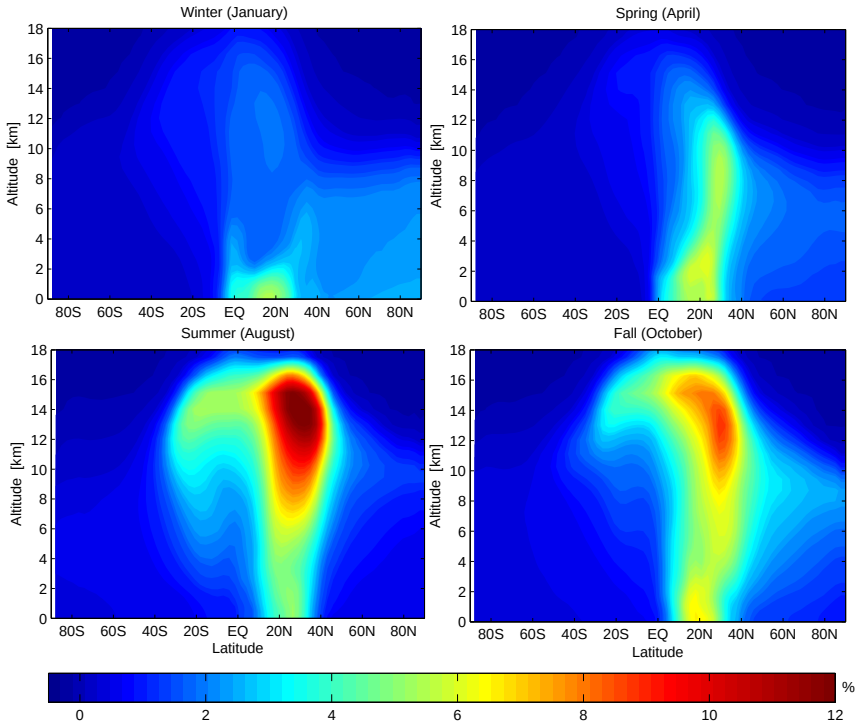

Figure 5.7: Relative change in ozone between emissions reperesenting 2008 and 2050 plottet as a zonal mean.

emissions at the surface that is increased, and naturally this is where. The second one is a result of the pollution at the surface being pumped up in the troposphere because of the large convection in summer. Up here the gases has a longer lifetime, and the ozone production continues. Looking at similar plots for CO and NO_2 (not shown here), they show a clear maximum in increase around 12-14 km, around the same height as the ozone concentrations show a second maximum

To give a better picture of the influence the increased emissions over India has in a global perspective, figure 5.7 shows the relative difference in ozone concentration plotted as a zonal mean. The over all pattern is fairly similar to figure 5.6, but the values are smaller as this is a mean. However, these plots shows a larger spread higher in the troposphere. The large scale circulation with air rising on the northern hemisphere, getting transported toward the north pole is clear, and for all seasons expect summer there is a increase of about 2-3% in the middle troposphere on the norther hemisphere. In both summer and fall there is a maximum, with an increase between 8-12% in the upper troposphere, a much higher increase than seen at the surface. This indicates that the increase just above India is more local, but the ozone that rises up to the middle and upper troposphere gets spread out over a much larger area as the transportation above the boundary layer is stronger. The relative increase over just above India at 80 degrees east (figure 5.6) is in fall around 10%, the same increase for the zonal mean (figure 5.7), meaning that the ozone at this level is fairly evenly spread out in east west direction and affects far beyond

India's borders. In the upper troposphere the transportation seems to be stronger to the south, but it don't seem to be able to transport the ozone beyond 40 degrees.

5.3 Calculating Change in Radiative Forcing

To be able to give a more exact answer to how much the change in ozone have affected the surface temperature I have calculated the change in radiative forcing using known equations, and the total change in tropospheric ozone. It is important to notice that these calculations don't take into account the height distribution in ozone. I have also calculated the change in radiative forcing and surface temperature from a change in the methane concentration using known equations and the change in methane lifetime.

5.3.1 Ozone

By calculating the mean of the global annual change in the ozone concentration of the total tropospheric column, you can calculate the change in radiative forcing, and from that give an estimate of the change in surface temperature. According to The IPCC fourth assessment report (*Denman et al.* (2007)), you can multiply this change in ozone concentration in expressed in Dobson units (DU) with 0,042 and get an estimate on the change in radiative forcing, this can again give an estimate on the potential change in surface temperature.

To calculate the total change in global ozone concentration in the entire troposphere, you need to take into account the different sizes of each grid box. Therefor it is necessary to weight the concentrations with respect to the area of each grid box for each month, before taking the average over the entire year to get a global annual mean change in the ozone column, $\mathcal{C}$:

$$\frac{\sum_{i,j,l}(concentration(i,j,l) * area(i,j))}{\sum_{i,j} area(i,j)} = C \tag{5.1}$$

$$\sum_{m=1}^{m=12} (C(m))/12 = \mathcal{C} \tag{5.2}$$

This has units $molecules/cm^2$, as this is the unit $Concentration(i,j,l)$ had, so I converted this to Dobson Units using the definition of Dobson:

$$1DU = 2,69 * 10^{16} moleculescm^{-2} \tag{5.3}$$

$$1moleculescm^{-2} = 1/(2,69 * 10^{16})DU \tag{5.4}$$

Doing these calculations I got $\mathcal{C} = 2.4242 * 10^{16}$, giving a global mean change in tropospheric ozone equal to 0,091 DU. The report concludes that the radiative forcing per O3 change ($Wm^{-2}perDU$) = 0,042, and with my change of 0,091 DU the change in radiative forcing as a result of increased ozone concentration in the troposphere will be:

$$\Delta F = 0,091DU * 0,042Wm^{-2}DU^{-1} = 0.003785Wm^{-2} \tag{5.5}$$

-

This can then be used to give an estimate on the increase in surface temperature, in *Jacob* (1999) they present a simplified expression for this:

$$\Delta T_0 = \lambda \Delta F \tag{5.6}$$

Where $DeltaT_0$ is the change in surface temperature, delta F is change in radiative forcing and λ is the climate sensitivity parameter, which when simulated using general circulation models is in the range of $0.3 - 1.4Km^2W^{-1}$. I therefor chose a number in the middle, and uses $\lambda = 0.8Km^2W^{-1}$. Substituting my ΔF in to this I get:

$$\Delta T_0 = 0,8Km^2W^{-1} * 3,785 * 10^{-3}Wm^{-2} = 3.028 * 10^{-3}K \tag{5.7}$$

Saying that the global change in surface temperature as a result of more ozone in the troposphere will lead to a increase in the surface temperature at approximately 0,003028 Kelvin. This is a small number, but it must be kept in mind that this is the global change in temperature that comes from an increase in the tropospheric ozone concentration as a result of an increase in anthropocentric emissions over India. If we looked at a case where we increased the emissions over the entire globe, and took into account the effects of all the different polluters we would probably get a different number. Still this tells us that the emissions from only a fraction of the world have the potential to change the climate on the entire globe..

5.3.2 Methane

As seen in chapter 2, section 2.3 ozone is an important source of OH, so when ozone concentrations is increased, this leads to a increase in OH. This could again lead to a decrease in methane lifetime and by that reduce the concentration of this greenhouse gas, as reacting with OH has shown to be the biggest sink for methane (*Jacob* (1999)). This could then potentially lead to a change in radiative forcing due to a change in methane concentrations in the troposphere. As for the increase in tropospheric ozone it is also possible to give an estimate on the change in radiative forcing as a result of changed methane concentration.

Because of methane's long lifetime (approximately nine years (*Jacob* (1999))), the potential change in concentration won't be seen when only running the model for three years. This means I can't cant look directly at the change in concentration, instead I used the change in the lifetime that is calculated by the model to give an estimate on how the concentration will change. I will also use mean values of today's concentration and the production to calculate this change.

You can express the change in concentration in the following way:

$$\frac{dC}{dt} = P - LC = P - C\frac{1}{\tau} \tag{5.8}$$

Where P stands for production, L is loss C is concentration, τ is the lifetime. Assuming that there is some sort of steady state, and that the change in concentration with time is equal to zero you can express the concentration c as:

$$C = \frac{P}{L} = P\tau \tag{5.9}$$

Using this you can find the change in concentration between the original run, and the one with emissions representing 2050:

$$\Delta C = P_{2050}\tau_{2050} - P_{2008}\tau_{2008} \tag{5.10}$$

$$\Delta C = P(\tau_{2050} - \tau_{2008}) \tag{5.11}$$

Assuming the production is the same for the two years. Today's concentration is given in Tg, meaning ΔC is expressed in Tg, so first I need to convert this to ppb. Using the same conversion factor as used in the IPCC (*Denman et al.* (2007)), we have 2,78 Tg CH_4 pr ppb. To find the 2050 concentration you add the change to the exciting concentration:

$$C_{2050} = C_{2008} + \Delta C \tag{5.12}$$

Substituting in values from IPCC fourth assessment report gives $P = 582tgy^{-1}$, $C_{2008} = 1745ppb$ *Denman et al.* (2007). The lifetimes calculated by the model shows $\tau_{2008} = 6.9449$ and $\tau_{2050} = 6.9656$, this gives a change in the methane concentration of $12.0474Tg = 4.3ppb$ and a new concentration for 2050 $C_{2050} = 1749.3ppb$.

To calculate the expected change in radiative forcing this gives, I used the formula presented in *Denman et al.* (2007):

$$\Delta F = \alpha(\sqrt{C_{2050}} - \sqrt{C_{2008}}) - (f(C_{2050}, N_0) - f(C_{2008}, N_0)) \tag{5.13}$$

Where the function f is defines as:

$$f(C, N) = 0.47ln[1 + 2.01x10^{-5}(CN)^{0.75} + 5.31x10^{-15}C(CN)^{1.52})] \tag{5.14}$$

And C is CH_4 concentration in ppb, and N is N_2O concentration in ppb. and $\alpha = 0.036$. As the model don't include N_2O, I used an estimate of 314 ppb presented by *Denman et al.* (2007). Further I substituted in the values for M and N giving $\Delta F = 1.6 * 10^{-3}$. This number must then be multiplied by 1.5 to account for the wrongful changes in concentrations of ozone from the lack in change of methane concentration (*Myhre et al.* (2013)). As OH increases so does the concentration of CH_3O2 from equation 2.4 in chapter 2, and by that the ozone concentration increases. In reality this won't happen as with time the concentration of CH_4 will get reduced an the concentrations of CH_3O2 will get reduced again. To compensate for this, studies have shown that you can multiply the change in radiative forcing with 1.5 *Myhre et al.* (2013). This gives a new ΔF:

$$\Delta F = 2.4 * 10^{-3}Wm^{-2} \tag{5.15}$$

The lifetime of CH_4 has increased slightly and so has the concentration. This means, and as the calculations show, that there will be a small increase in the radiative forcing from CH_4. In the model methane is predefined by climatological means, meaning the concentrations is the same in both model runs. The reason for the increase must then be because of a smaller chemical loss, as methane has no chemical sources in the troposphere. Knowing that reaction with OH is the largest sink of CH_4, this means that it is a net decrease in OH concentrations when the anthropocentric emissions is increased. Plotting the change in OH concentration in the troposphere (not shown here) shows that this is the case, except from just above India and the ares close, there is a relative decrease in OH over larger part of the northern hemisphere depending on the season. This is probably because reaction with OH is also the primary sink for CO (*Logan et al.* (1981)), so when increasing the emissions of CO by 140% this will also increase the loss of OH. We therefor see a net loss of OH, despite the large increase in ozone production, resulting in a increase in methane lifetime and concentration.

To estimate what the change in surface temperature this change indicates, I use the same formula used I used when calculating surface temperature change for ozone: $\Delta T_0 = \lambda \Delta F$ (*Jacob* (1999)), giving:

$$\Delta T_0 = 0,8 K m^2 W^{-1} * 2.4 * 10^{-3} W m^{-2} = 1.92 * 10^{-3} K \tag{5.16}$$

This means that as a result of increased methane lifetime, and by that increased methane concentrations it will be a global increase in surface temperature of 0.00192 K. This is, as for the change we saw from the change in ozone concentration a small number. But putting it into perspective, this is the total increase in global surface temperature as a result of just the increase in methane concentration from a increase in emissions only over India.

Chapter 6

Discussion

In this chapter I will discuss results presented in the previous chapter and look at how the change in emissions will affect the air quality over India, and what consequences this increase could have on humans and vegetation. I will also look at what we need to keep in mind when looking at results from climate models, and how both direct and indirect effects that's not being taken into account when running climate models potentially can affect the results.

6.1 Surface Concentrations

When looking at how the perturbed emissions has affected the ozone concentration at the surface I have looked at both the relative and absolute change in ozone concentration to be able to say something about where the change in emission has the largest impact on the environment and air quality at the surface. Where the total emission of ozone precursors is the highest is not necessary where an increase in emission will affect the ground concentration of ozone the most. This can be seen in figure 6.1, the absolute increase in ozone concentration don't follow the same pattern as the absolute increase in the concentration of NO_2 and CO (figure 5.1 and 5.2). Figure 6.2 and 6.1 shows the relative and absolute increase in ozone concentration between the model run using 2008 emissions, and the one with perturbed emissions representing 2050 for the four seasons at 0.01 km height.

For January we find the largest increase in ozone at the same locations where the concentrations already was at it's highest, and as mentioned in the previous section, the ozone distribution with 2050 emissions is similar to the one for 2008. The relative increase has a little different pattern, and in figure 6.2 we see a increase around 40-50% in the southern part of India blowing out over the Arabian Sea, while over 27 degrees north the increase is only about 10%. Looking at the relative increase in CO and NO_2 (not shown here) we see a more even evenly relative increase over the entire continent, and the dividing in increase is not seen. This means that there is another explanations for the geographical difference in relative increase in ozone. One explanation could be that the emissions further north, is already so high, that an increase don't have as much impact on the ozone production, it's already saturated, and the top of the "ozone production curve" seen in figure 2.3 in chapter 2 is reached. We do know from satellite observations shown in figure

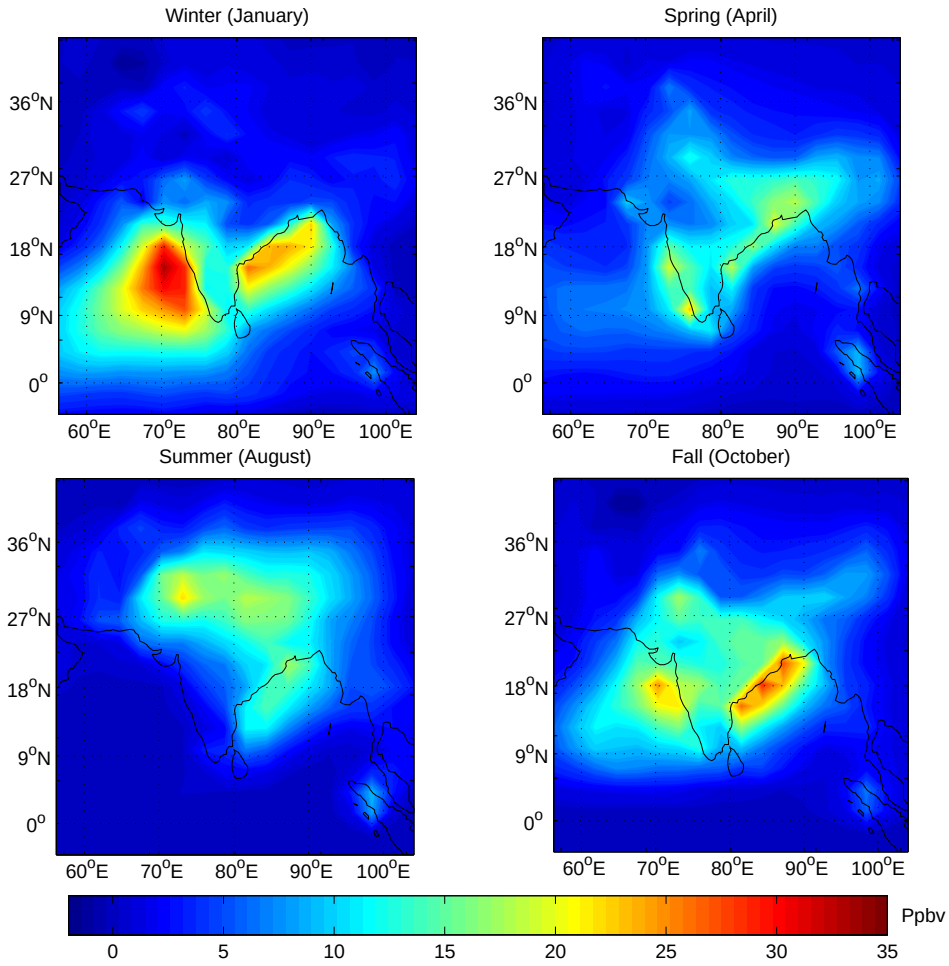

Figure 6.1: Absolute difference in ozone concentration in ppbv for the different seasons at 0.01km height.

4.8, chapter 2 that IGP is the region with the largest concentration of CO and NO_2, so this could be a good explanation. Another reason could be that winter is the time of year with the weakest incoming solar radiation, with less radiation in the north compared to further south. But if this was the only reason, one would expect a more diffuse transition between the two regimes. To decide if it is the one or the other, or a combination of the two, more research would be needed. For example a sensitivity test, reducing the increase in NO_x emissions, and see if this lead to the same increase in ozone. If that is the case, it is likely that it is the non-linearity in the ozone production that's the explanation. There is also a small decrease in ozone in the upper left corner of the figure, in this same location we saw a absolute increase in NO_2 by about 8 ppbv, and the decrease is probably a result of NO_x-titration of ozone as explained in chapter 2.

During spring we see a large relative increase in ozone at 40-50% along the coastlines, and also over the IGP, a pattern similar to the absolute increase. The largest increase is seen over

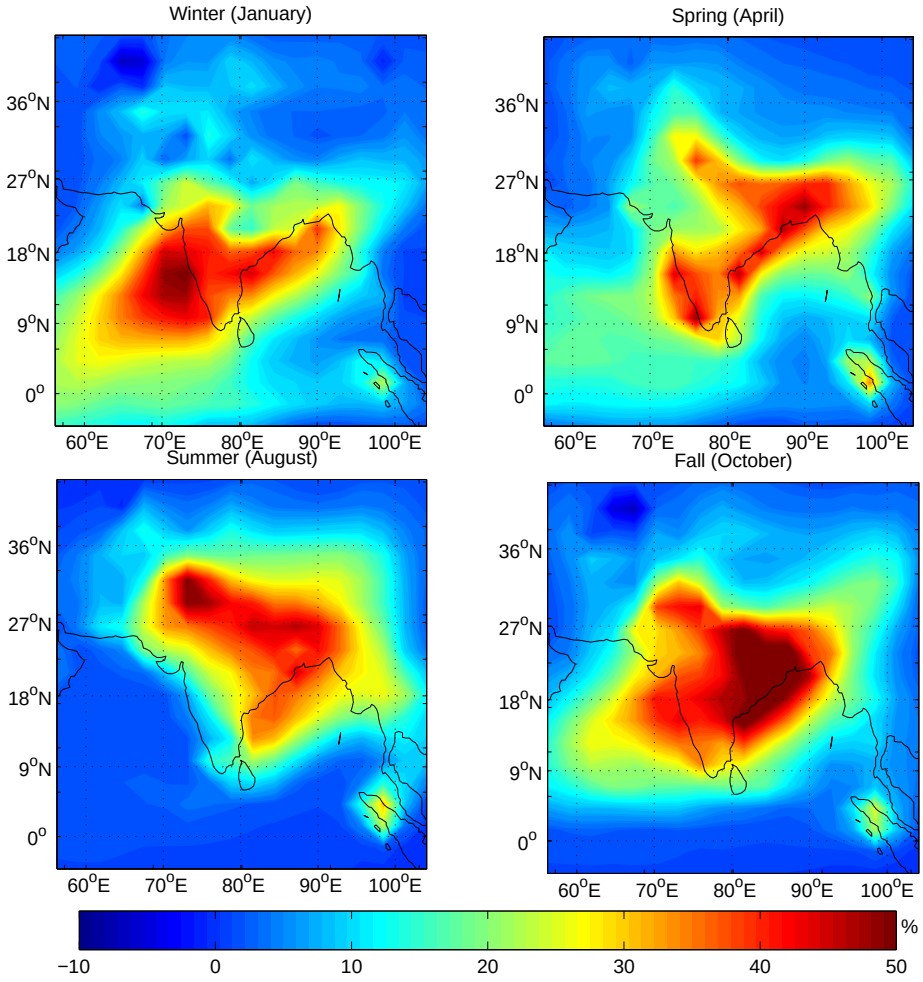

Figure 6.2: Relative change in ozone concentration in ppbv for the four different seasons at 0.01km height.

coast as the winds blow on shore in spring, this has led to relatively high surface concentrations in ozone over the entire continent. Figure 5.3 shows values at around 50 ppb over most of India.

In summer we still see the monsoon decreasing the ozone concentration, and we only get a small increase in ozone on the west coast of about 10%. Further north where the amount of rainfall (*IMD* (2009)) is less, we get a large increase in ozone concentration as high as 50% over New Delhi. Meaning we get the highest concentrations over land, at about 65-75 ppbv just north of the IGP and over New Delhi. Summer is the season with the lowest ozone concentration as a result of lower emissions, and lower incoming solar radiation because of the monsoon. So a high relative increase don't necessarily mean that the absolute increase is very large, so the increase concentrations further south, and at the west coast where the monsoon comes in from the ocean is not as big, and the absolute increase is only at about 5 ppbv. But when looking at figure 5.3 will this increase give the highest values observed over land further north, with a absolute increase at

WHO air quality guideline and interim target for ozone: 8-hour concentrations

	Daily maximum 8-hour mean ($\mu g/m^3$)	Basis for selected level
High levels	240	Significant health effects; substantial proportion of vulnerable populations affected.
Interim target-1 (IT-1)	160	Important health effects; does not provide adequate protection of public health. Exposure to this level of ozone is associated with: • physiological and inflammatory lung effects in healthy exercising young adults exposed for periods of 6.6 hours; • health effects in children (based on various summer camp studies in which children were exposed to ambient ozone levels). • an estimated 3–5% increase in daily mortality[a] (based on findings of daily time-series studies).
Air quality guideline (AQG)	**100**	Provides adequate protection of public health, though some health effects may occur below this level. Exposure to this level of ozone is associated with: • an estimated 1–2% increase in daily mortality[a] (based on findings of daily time-series studies). • Extrapolation from chamber and field studies based on the likelihood that real-life exposure tends to be repetitive and chamber studies exclude highly sensitive or clinically compromised subjects, or children. • Likelihood that ambient ozone is a marker for related oxidants.

[a] Deaths attributable to ozone. Time-series studies indicate an increase in daily mortality in the range of 0.3–0.5% for every 10 $\mu g/m^3$ increment in 8-hour ozone concentrations above an estimated baseline level of 70 $\mu g/m^3$.

Figure 6.3: Table of WHO air quality guidlines for ozone given as 8-hours concentrations. For ozone $2\mu g/m^3$ = 1 ppb. The table is taken from *WHO* (2006)

around 15-20 ppbv.

In fall the monsoon is over, and we see a relatively even increase in the ozone concentration around 40-50%, this is the season with the largest relative increase and also the largest surface concentrations of ozone. The winds blow offshore, so there is also a relative increase in ozone over the oceans.

6.1.1 Air Quality and Consequences

My results show that with a worst case scenario for the increase in anthropogenic emissions the ozone concentrations at the surface will increase with up to 50%, resulting in average ozone concentrations at around 50 ppbv, and for some areas up to 75 ppbv. As these values are monthly averages, concentration during mid-day will be much higher, as this is the time of day with maximum incoming solar radiation, end therefor maximum ozone production, and minimum during night (chapter 2, section 2.1). According to the guidelines made by WHO (World Health Organization) spending a maximum of eight hours in ozone concentrations under 50 ppb is considered safe, although health impacts has been seen under this level, this is the official recommendation *WHO* (2006).

Figure (6.3) shows the air quality guideline table for ozone made by WHO, and shows the

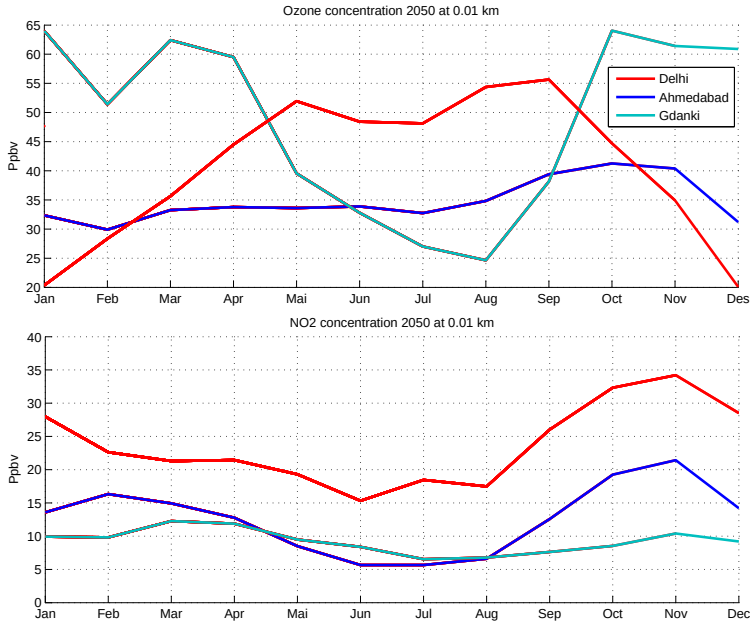

Figure 6.4: The modeled NO_2 and O_3 concentration with emissions reperesenting the year 2050 two Urban locations (Ahmedabad and Delhi) and one rural (Gdanki) plotted as a timeseries.

interim target for ozone given in micro gram per cubic meter for 8-hour concentrations together with the basis for the different levels. Translated into ppb we can read from this that spending 8 hours or more in concentrations over 80 ppb could lead to health effect on children, damage on the lungs on healthy young adults and an increase of 3-5% in the mortality.

The upper figure in figure 6.4 shows seasonal variation in ozone concentration at 0.01 km for two urban (Delhi and Ahmedabad) and one rural location (Gdanki), with emissions representing 2050. The model has shown to simulate the concentrations at this level for both urban and rural locations well (chapter 4, section 4.1) lending confident into that these plots is reasonable. The highest values is seen over Gdanki, the only rural location of the three, with monthly averages at over 60 ppb. This means that the ozone concentrations during the day probably will exceed 80 ppb, and interim target-1 set by the WHO, and will can severely hurt public health. So for all the cites in this plot the ozone concentration can be expected to exceed WHO air quality guidelines for adequate protection of public health.

Ozone has also shown to be toxic to vegetation, and an increase in surface level of ozone may have significant adverse effect on the global food production and ecosystem (*Ashmore* (2005)). According to a study from 2013 (*Tang et al.* (2013)) there was a estimated wheat production loss at 8,2-22,3% in India already in 2000 as a result of increased ozone concentration. According to these predictions for the 2050 surface concentration of ozone, severe damage on vegetation is expected. To prevent this number to get even larger, measures needs to be taken, as for example develop wheat that is more resistant to ozone.

The large increase in NO_2 concentration might also be a health problem at it's own, according to WHO large NO_2 concentration can lead to a number of negative effects on the lungs, as for example respiratory symptoms on infants, and bronchitic symptoms on asthmatic children (*WHO* (2006)). It is unclear if these symptoms is just a result of NO_2, or if secondary combustion-related products also needs to take a part of the blame, but this is not a risk worth taking. With a absolute increase between 12-20 ppbv the total concentrations of NO_2 over IGP will be over 30 ppbv in the larger cities. The WHO has set a annual mean guideline of 40 $microgram/m^3$, which is equivalent to approximately 21 ppbv (*WHO* (2006)). This means that living in NO_2 concentrations higher than 20 ppbv is considered bad for human health.

Figure (6.4) illustrates what NO_2 values that could be expected over large cities with emissions representing the year 2050, this is a time series plot showing the seasonal variations in surface concentrations of NO_2 over to urban (Delhi and Ahmedabad) and one rural (Gdanki) location in India. Looking at this figure, and taking into account that the validation for surface concentration of NO_2 in chapter 4, section 4.1 showed that the modeled NO_2 concentrations during winter in urban areas where underestimated, and in general overestimated over rural locations. We can probably expect even higher concentrations in winter for the two urban cites, and the limit set by the WHO will be exceeded. Meaning that pollution by NO_2 can potentially be a large health issue in the cities in India if no precaution is taken, and the emissions reaches a worst case scenario.

6.2 Change in Radiative Forcing

From the pot of vertical sections in the previous chapter it's clear that an increase in surface emissions in India will increase the ozone concentrations in the entire troposphere, and across larger parts of the globe. Especially in summer and fall when the convection is more powerful, and ozone from the surface gets transported higher up in the troposphere. Here the winds are stronger, and the ozone gets transported out outside of India's borders potentially increasing the radiative forcing on larger parts of the globe.

As mentioned in the introduction to this chapter, weather an increase in ozone concentration leads to a change in radiative forcing and surface temperatures or not depends on where in the troposphere the increase is located. The temperature difference between the surface and the absorbing layer radiating to space is decisive. How well a gas absorbs radiation depends on how much of the gas that already is present, and how many other gasses that absorb the same wavelengths. You also need to take into account the indirect effects a increase in pollution will have, as for example a change in surface temperature or ozone concentrations could effect the vegetation and again effect the emissions.

Several studies have shown that an increase in ozone concentrations higher up in the troposphere has a larger effect on the surface temperature, than an increase closer to the surface (*Lacis et al.* (1990)). A study by Fosters and Shine shows that with a ten per cent increase in ozone concentration at the different levels, the largest effect on the surface temperature is when the increase is between 5 and 15 km, with a peak at around 11 (*de F. Forster and Shine* (1997)). This is shown in figure 6.5. My zonal mean shows an increase at around 10% in this region in both

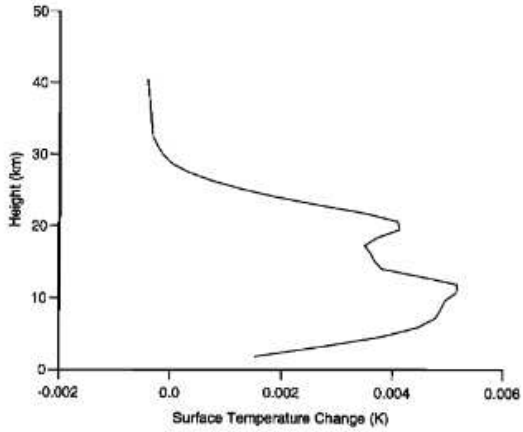

Figure 6.5: The change in surface temperature (Kelvin) as a function of height of ozone change. The figure was produced by increasing ozone concentrations by 10% in each 1 km thick layer of the atmosphere in turn. Results are from a radiative-convective model and are for the global mean atmospheric profile. No atmospheric feedback are included. The figure is taken from *de F. Forster and Shine* (1997)

summer and fall, and based on this figure an increase in the surface temperature will be expected.

This is only a rough estimate to try and say something about whether or not the increase we see in the ozone concentrations will affect the radiative forcing. So by using this figure (6.5) as reference, the increase in ozone seen over over India, and the rest of the world as a result of increased emissions will lead to a increase in surface temperature.

Calculations supports what we saw from the figures, there will be a increase in the radiative forcing and surface temperature as a result of increased ozone concentrations. There will also be a small increase in the radiative forcing as a result of increased methane.

6.3 Limitations of My Results

When looking at these results and calculations it is important to keep in that mind there is some factors in both the model, and choices made by me, that can affect the results. So when discussing it's important to remember that this is only one aspect of a much bigger picture. There are several indirect effects that needs to be taken into account to give a more exact estimate on how this increase in anthropogenic emissions will affect the radiative forcing and surface temperature. There is also some direct effect that's not included in the model, but these are also important to keep in mind when looking at the results.

In both model runs I use meteorological data for 2008, chances are that the meteorological situation over India in 2050 is different from the one we have today. And as seen in chapter 2, both temperature, incoming solar radiation and wind pattern have a large effect on the ozone concentration in the troposphere. For example could a weakening of the monsoon lead to increased

incoming ozone concentrations during summer as a result of increased solar radiation. With a change in wind patterns the geographical distribution of pollution could change, and this could again affect the ozone concentration. Figure 2.4 in chapter 2 shows how large effect the wind pattern has on the ozone distribution along the coast, and a weakening in the wind blowing off shore would mean increased ozone concentration over the continents, and a decrease in ozone concentration over the ocean.

Vegetation plays also an important role in the loss mechanism of ozone, this links closely to a potential change in the meteorology. Take for example a weakening in the monsoon, this increases the incoming solar radiation, and reduces the rainfall. In dry weather the plants stomata closes to protect the plants against desiccation, and the dry deposition get reduced, leading to additional increase in surface ozone (*Fowler et al.* (2005)). Agriculture could also change, which mean a change in how the soil is used either by reducing or increasing the areas used for farming, or by a change in what they are growing. This can affect the biogenic emissions, or change the dry deposition to the ground. The direct effect ozone has on vegetation will have an indirect effect on the climate, and can lead to increased heating. Surface ozone will damage the vegetation *Ashmore* (2005), and this leads a increase in atmospheric CO_2 as less is consumed by the vegetation. Some calculations show that this indirect effect is as large as, or even bigger than the direct radiative forcing from ozone (*Sitch et al.* (2007)). A dryer climate in general could also lead to more forest fires, this will lead to an increase in the emissions.

The stratosphere plays an important role with respect to change in both shortwave and thermal infrared radiation reaching the troposphere, and ozone exchange across the tropopause. For this study the stratospheric chemistry is turned off, so these interactions will be lost in my calculations. The temperature of the stratosphere effects the chemistry happening there, and this could then affect the concentrations of the gases transported down to the troposphere.

A larger change in climate in general, could lead to a change in both the emission from lightning and biogenic, and increasing convection would lead to an increase in lightning, and by that an increase inÂ NO_x emissions. Looking at the bigger picture, and a change in climate all over the globe there is a large possibility of a change in the large scale circulation patterns as the Brewer Dobson circulation. Smaller temperature differences between equator and the poles would weaken the transport fluxes between the stratosphere and the troposphere. For India this would mean a smaller flux of ozone being transported up into the stratosphere, and a increased level of ozone in the middle to upper troposphere.

Chapter 7

Conclusion

In the theory chapter (chapter 2) we saw that the chemical production and destruction of tropospheric ozone is highly dependent on the photo-chemical activity and the concentration of ozone precursors as CO, NO_x and VOC. Increased emissions will in most cases lead to increased production of ozone, except from when we get NO_x-titration, reducing the ozone concentration with increasing NO_x values (chapther 2). The meteorology plays also a big part with regards to the ozone concentration in India, weather the winds are blowing on-shore or off-shore is very important when looking at geographical distribution. The ozone production increases with increasing solar radiation, summer is the time of year with the highest incoming solar radiation but because of the monsoon we get the largest ozone concentrations during spring. The summer monsoon is important in reducing the ozone concentration as the cloudy, rainy conditions reduces the incoming solar radiation, increases the dry deposition and the winds are blowing on-shore transporting clean marine air over the continents (chapter 2, section 2.2).

When increasing the anthropogenic emissions of NO_x with 150%, and CO and VOC with 140%, a worst case scenario from the IPCC report for 2050, it will lead to a increase in surface ozone with up to 50% (figure 6.2). The highest relative increase is seen over the IGP, creating ozone concentrations as high as 65-75 ppbv in this region. We also see a similar high increase in spring over most of the continent, creating a relatively even ozone concentration at around 50 ppbv over the continent (figure 5.3). The WHO recommendations for air quality states that spending more than 8 hours daily in concentrations above 50 ppbv is considered dangerous for your health (*WHO* (2006)), given that the values presented here is monthly means this limit will be exceeded over most of India. Increasing the ozone concentrations will also lead to increased damage on crops, and hurt the vegetation (chapter 5, section 6.1.1).

When increasing the NO_x emissions with 150%, this results in surface concentrations of NO_2 above 20 ppb over Delhi, and around 10-15 ppb for the smaller city Ahmedabad and rural Gdanki (figure 6.4). The annual mean guideline set by the WHO for air quality is 21 ppb (*WHO* (2006)), meaning the large increase in NO_x emissions will also be bad for human health.

This increase in emissions will also change the radiative forcing as a result of increased ozone and methane concentrations. These increases will not only affect the surface temperature over

India, but affect the entire globe.

The increase in pollution at the surface will be transported up in the troposphere, especially during summer when there is more convection. We see that ozone already produced at the surface is transported up to the tropopause in both summer and fall, the same goes for the ozone precursors, continuing the production of ozone higher up in the troposphere (chapter 5, section 5.2.2). This affect the radiative forcing, and lead to increased surface temperatures. This increase in emissions will also lead to a decrease in available OH, which leads to an increase in methane lifetime, as reacting with OH is the main sink for methane. This results in increased methane concentrations in the troposphere, and this will also increase the radiative forcing, and result in slightly higher surface temperatures (5, section 5.3).

Calculation shows that there will be a global increase in radiative forcing at $0.003785 Wm^{-2}$ as a result of increased ozone, which corresponds to a increase in surface temperature at approximately $3.028 * 10^{-3} K$. Same type of calculations done for the change in methane concentrations give a increase in radiative forcing at $2.4 * 10^{-3} Wm^{-2}$ resulting in a temperature change of approximately $1.92 * 10^{-3} K$ (chapter 5, section 5.3).

These results tells us that if no measures is taken to reduce the emissions over India the air quality will be harmful for both human health and vegetation, not only in the large cites, but the pollution will spread out to more rural locations. It will also lead to a change in radiative forcing, and increased surface temperatures. An increase in pollution in India will be very harmful for both humans and agriculture with respect to surface air quality, but it could also affect radiative forcing both over India and on the entire globe.

Based on my findings there is more research that can be done to get a better picture of the situation, and what needs to be done to reduce the high concentration of pollution over India. I have four main points I think should be looked more closely into:

- To get a better picture of the surface concentrations it could be useful to try and run the model with higher resolution. The coarse resolution of Oslo CTM3 have problems dissolving local feature, and it dilutes out the concentrations i highly polluted cities, and rural areas are very sensitive to the influence of a city lying in the same grid. So to look more closely into air quality, and surface concentrations of ozone, and especially NO_x, higher resolution is needed.

- A study looking into what different cuts in emissions would be helpful to improve the air quality, and where future precautions will have the largest impact. The NO_x-titration can for example lead to a increase in ozone concentration if you only cut NO_x concentrations and not VOC. This is illustrated in figure 2.3 in chapter 2. So to do some sensitivity tests, where you tried to reduce the different gases you could get a picture of where it will be most effective to cut.

- It could also be interesting to try and run a climate sensitivity model to get a more exact result on how the increased emissions affect the global radiative forcing, and change in surface temperature. In my study I have only looked at the effect of two separate processes,

so to do a more conclusive study and include more of the indirect effect as a temperature change in the stratosphere, and how a potential temperature change will affect the ozone concentrations could be interesting. This could give a better picture on the importance of emissions control in the entire world, and that only reducing the emissions in the western countries is not enough to "save he world".

- With today's climate it's thanks to the monsoon that the ozone concentrations in summer is as low as we see today, but if the climate changes and the monsoonal season weakens this could mean increased ozone concentrations in summer. So a study looking at how a break in the monsoon will effect the ozone concentrations, could be interesting also for examining what the effect incoming solar radiation has on the ozone production.

Appendix A

Appendix

Table 9: The components of the tropospheric chemistry application. The table gives order of magnitude estimates of the lifetime of the components. If the lifetime is short, there is no need for transport.

Nr	Component name	Remarks	Approximate lifetime	Transport	Wet dep.
1	O_3		~ months	Yes	Yes
4	HNO_3		~ weeks	Yes	Yes
5	PANX	PAN + CH_3CO_3		Yes	No
6	CO			Yes	No
7	C_2H_4	Ethene		Yes	No
8	C_2H_6	Ethane		Yes	No
9	C_3H_6	Propene [CH_3CHCH_2]		Yes	No
10	C_4H_{10}	Butane [$CH_3CH_2CH_2CH_3$]		Yes	No
11	C_6H_{14}	Dimethylbutane		Yes	No
12	C_6HXR	methyl-benzene		Yes	No
13	CH_2O	Formaldehyde		Yes	Yes
14	CH_3CHO	acetaldehyde		Yes	Yes
15	H_2O_2	hydrogenperoxide		Yes	Yes
16	CH_3O_2H	methyl hydroperoxide		Yes	Yes
17	HO_2NO_2			Yes	Yes
18	CH_3COY	Bi-acetyl [$CH_3COCOCH_3$]		Yes	No
19	C_3COX	Methylethyl ketone (2-butanone), $CH_3COC_2H_5$		Yes	No
20	ISORPRENE	Isoprene/2-methylbuta-1,3-diene [C5H8]		Yes	No
21	HO_2		short	Maybe	No
22	CH_3O_2	methyldioxy radical	short	No	No
23	$C_2H_5O_2$	ethyldioxy radical	short	No	No
24	$C_4H_9O_2$	butyldioxy radical	short	No	No
25	$C_6H_{13}O_2$		short	No	No
27	CH_3COB	RO_2 from C_4H_{10}+OH, $CH_3COCH(O_2)CH_3$		Yes	No
28	CH_3CXX	$CH_3CH(O_2)CH_2OH$		Yes	No
29	AR1	RO_2 from C_6HXR + OH	short	Maybe	No
30	AR2	Ketone from AR1		Yes	No
31	AR3	RO_2 from AR3	short	Maybe	No
32	ISOR1	RO_2 from ISOPRENE + OH	short	Maybe	No
33	ISOK	methylvinylketone + methacrolein (ketones)		Yes	Yes
34	ISOR3	RO_2 from ISOK	short	Maybe	No
35	HCOHCO	Glyoxal		Yes	No
36	RCOHCO	Methyl glyoxal, CH_3COCHO		Yes	No
37	CH_3X	Peroxyacetyl radical, CH_3CO_3		Yes	No
38	$O(^3P)$		short	No	No
39	$O(^1D)$		short	No	No
40	OH		short	No	No
41	NO_3			Yes	No
42	N_2O_5			Yes	No
43	NO			Yes	No
44	NO_2			Yes	No
46	CH_4	Methane	~ years	Yes	No
48	C_3H_8	Propane		Yes	No
49	$C_3H_7O_2$	Propyl peroxide; from (propane+OH)+O_2		Yes	No
50	Acetone	CH_3COCH_3		Yes	No
51	C_3COD	Propyldioxy, 2-oxo-propyldioxy, $CH_3COCH_2(O_2)$		Yes	No

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